CYCLOPENTADIENYLIDES AND NONBENZENOID AROMATICITY

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## ABSTRACT

Several cyclopentadienylides and three new derivatives of triphenylphosphoniumcyclopentadienylide have been prepared and examination of their nmr spectra showed that the proton chemical shifts of the cyclopentadienylidene system are in the region expected for such nonbenzenoid aromatic systems. Some of the ylids have been shown to undergo electrophilic substitution reactions and protonations in the negatively charged cyclopentadiene moiety in accordance with the chemical criterion for the aromatic character of the five-membered ring. From the evidence available so far, it would seem that in triphenylphosphonium and trimethylammoniumcyclopentadienylides, electrophilic attack in the five-membered ring takes place preferentially in the 2-position.

Several new reactions of triphenylphosphoniumcyclopentadienylide have been discovered and the structures of the products of these reactions have been established. The ir, uv and nmr spectra of these compounds are discussed. The sites of protonation in these derivatives as well as some other ylids have been established by examination of the nmr spectra of these compounds in trifluoroacetic acid.

Some aspects of the chemistry of these compounds including dipolar addition reactions and attempts at generating novel nonbenzenoid aromatic systems, as well as aspects of the mechanism of formation of these ylids and some of their derivatives are discussed.

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# INTRODUCTION

Kekule first published his views on the structure of aromatic
compounds over a century ago. Since then, aromatic compounds have
provided the chemist a multitude of fascinating and intriguing problems.
Benzene was the aromatic compound par excellence. Over the years, the
term "aromatic" was regarded as synonymous with "benzenoid" (i.e. a
derivative of benzene) but, it soon became apparent that the structures
and reactions of many unsaturated heterocyclic compounds were similar
to those of benzene derivatives. Thus the term aromatic acquired a
diffuse meaning to include structural features (i.e. the presence of a
benzene ring) as well as chemical properties (i.e. properties
resembling those of benzene).

The expression "aromatic character" was adopted many years
ago to summarize the chemical behavior of 'aromatic' compounds and
chemists began using it in different connotations to suit individual
interests, the generally accepted criteria being the benzene-like
stability and chemical properties and the cyclic structure of the
compounds. Soon the term "aromaticity" crept into the vocabulary of
organic chemists. It is uncertain how and under what circumstances the
term was first introduced. Nevertheless, the need for such a concept
was recognized along with an outburst of research in this field.

It became highly desirable to put "aromaticity" or "aromatic
character" on a more quantitative level. Physical methods for the
study of cyclic compounds have been improved, new techniques have been
devised and new evidence has been forthcoming. In the last two or three
decades, many new non-benzenoid compounds, monocyclic as well as

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polycyclic, have been synthesized and studied. The publication of various recent monographs and reviews devoted to the problem of "aromaticity" is a clear indication of the high interest in this field[1-6].

The lack of clarity and brevity which still surrounds the concept of "aromaticity" has been well brought out by W.D. Ollis when he wrote: "No satisfactory and generally acceptable definition of the term 'aromaticity' has been given but one doubts if this is necessary. We all know (or do we know?) what 'aromaticity' means but this has not inhibited the use of new terms such as pseudo-aromaticity, non-benzenoid aromaticity, homoaromaticity, antiaromaticity and even antihomoaromaticity..."[7] Any definition of "aromaticity" in terms of "aromatic character" (i.e. using chemical reactivity and stability as the criteria) is open to serious criticism because stability and reactivity are not functions of the molecule in the ground state but are functions of the free energy differences between the ground states and the transition states of the processes involved. When this free energy difference is small, the compound is reactive regardless of the energy content in the ground state. In 1959, Sir Robert Robinson wrote: "The most logical procedure would be to identify the structural (electronic) factors which determine "aromaticity" and then base our classification on their presence, with due attention to the gradations of phenomena. It must be understood that "aromaticity" is never 100 per cent and the quality may be but feebly exhibited".[8]

As early as 1925, Robinson pointed out, with characteristic insight into the problem, that the aromatic character of benzene and its derivatives was due to the association of six valence electrons.[9] Such

association, it was reasoned, conferred a degree of enhanced stability

to the system. This association of six electrons, symbolized by a circle,

was termed the "aromatic sextet". The concept of the aromatic sextet was

soon extended to explain the aromatic character of heterocyclic compounds

like pyrrole, thiophene, pyridine etc. This also gave a rational

explanation for the stability of the cyclopentadienyl anion $(C_5H_5)^-$, which

has six electrons shared among the five equivalent CH groups in the

ring as shown below:
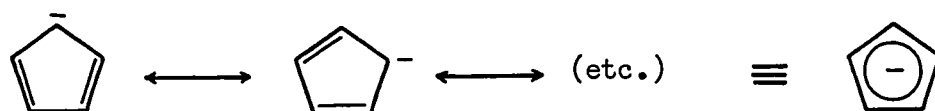
Later the concept of aromatic sextet was employed to predict new kinds

of aromatic structures and many of these ideas were rapidly justified by

syntheses. For cyclic structures the inscribed circle notation

symbolizing a sextet of π-electrons has been widely adopted[10] as

illustrated in the cases of benzene (I), pyridine (II), pyrrole (III),

thiophene (IV), cyclopentadienide anion (V) and cycloheptatrienium

cation (VI)*.

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* According to the currently accepted convention an inscribed full circle
is used for a delocalized system of six π-electrons; dotted or broken
circles are used for delocalized stable systems of other than six π-
electrons (cf. ref.2, pp 10-11). Any charges associated with the system
are shown inside the circles. For a criticism regarding the all too
convenient use of the circle symbol for the aromatic sextet, especially
for polycyclic systems, see ref. 4, p 47.

I        II        III        IV        V        VI
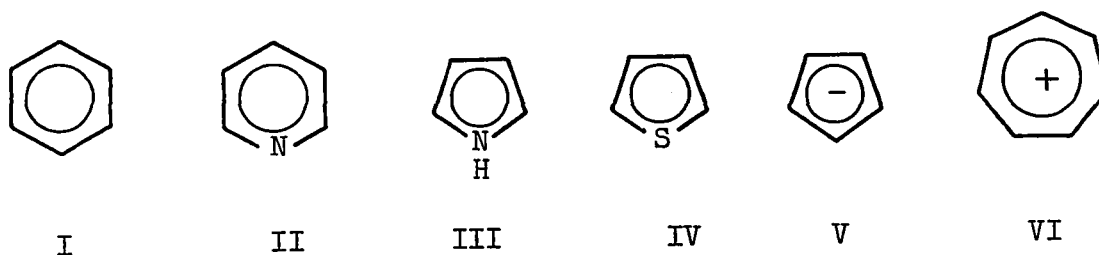
In 1925, not only was the concept of the aromatic sextet

recognized as a specially favorable number of electrons, but it was also

thought that other groups of electrons made up of other numbers of

electrons might not have this same stability: "The unsaturated nature of

cyclooctatetraene suggests that a stable group of eight electrons

analogous to the aromatic sextet is not formed."[9]   However, during

1931-1938, Huckel developed the basic pattern of the molecular orbital

theory of unsaturated and aromatic compounds.  The interesting conclusion

of this theory was that for any planar monocyclic system the binding

energy would vary with the number of $\pi$-electrons, and that systems

containing $(4n + 2)$ $\pi$-electrons (where n = 0, 1, 2, 3, 4.....etc.) would

be particularly favored.  This has emerged as the now famous Huckel's

Rule according to which "monocyclic coplanar systems of trigonally

hybridized atoms which contain $(4n + 2)$ $\pi$-electrons possess special

aromatic stability".

It can be seen that the aromatic sextet is a particular case of

this general rule (n = 1).  It also means that planar systems having

2, 6, 10, 14, 18....etc. $\pi$-electrons must also possess aromatic character.

The Huckel Rule soon provided a challenge to the imagination and skill

of the synthetic organic chemist as a molecular architect. An outburst
of research in this area followed to examine the validity and scope of
Huckel's Rule. A wide variety of novel non-benzenoid aromatic systems,
both monocyclic and polycyclic have been synthesized and studied. The
rule has stood the test remarkably well.

In Huckel's molecular orbital (HMO) treatment, the $\pi$-electrons
of the cyclic conjugated system are regarded as common to all the atoms of
the system and are considered to occur in common molecular orbitals.
Three types of molecular orbitals are defined, viz., <u>bonding orbitals</u>
(where the energy of the electrons is less than their energy in atomic
orbitals; consequently the occurrence of electrons in these orbitals
makes the system more stable), <u>non-bonding orbitals</u> (where the energy of
the electrons is considered to be the same as in the atomic orbitals),
and <u>anti-bonding orbitals</u> (where the energy of the electrons is greater
than their energy in the atomic orbitals; consequently occurrence of elect-
rons in these orbitals makes the system less stable). The numbers of
each of these kinds of orbitals and their energies for any particular
conjugated system depend on the number of atoms which make up the system
and the symmetry properties of the system. The results of the HMO
treatment for three simple carbocyclic systems, benzene, cyclopentadiene
and cycloheptatriene are shown in Fig. 1.

The important fact that emerges from Fig. 1 is that in each
case the ground state has three bonding orbitals, and when the Pauli
principle is taken into account, contains a stable "closed" shell* of

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* A "closed" shell of electrons is a system in which either removal of
electrons or addition of further electrons increase the total energy of
the system and consequently diminishes its stability.
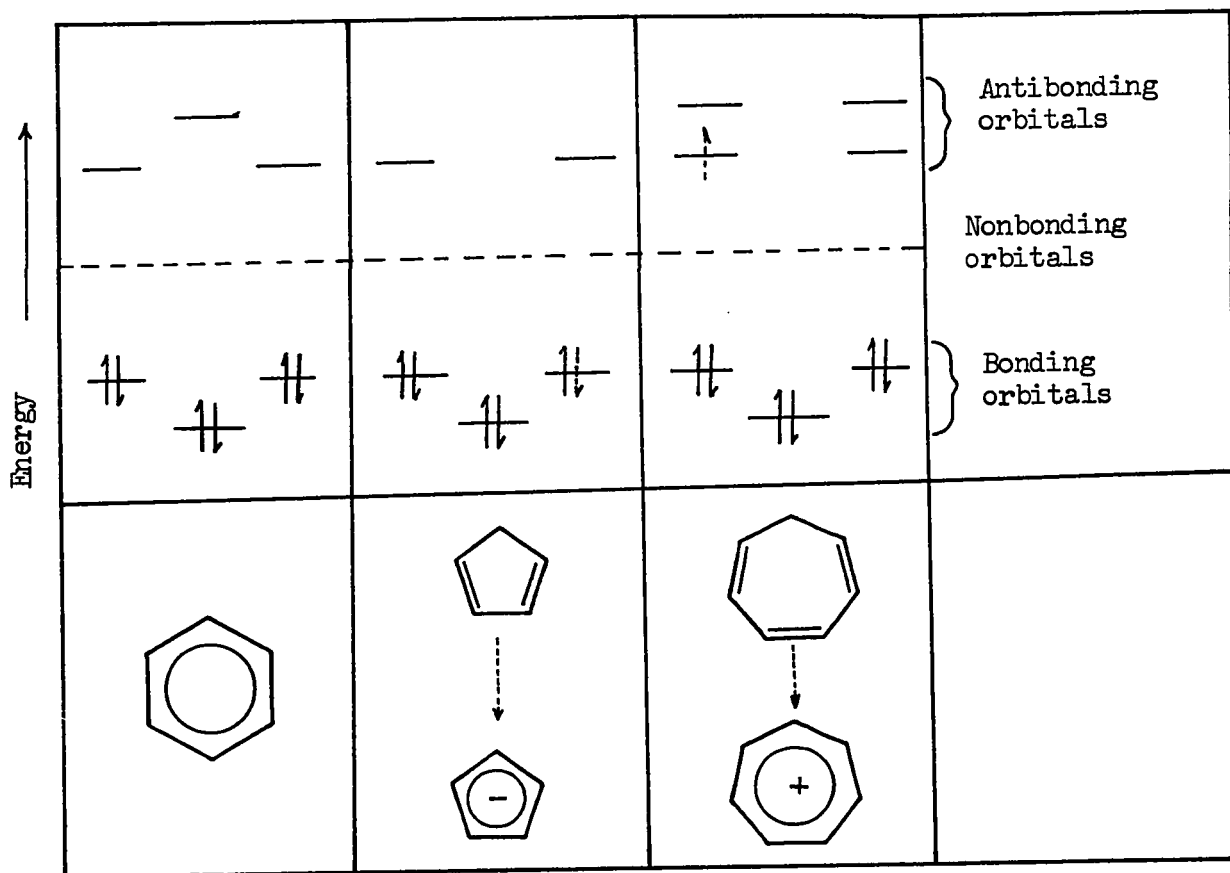
Fig 1.

six $\pi$-electrons. Hence the tendency of cyclopentadiene to take up a sixth electron to form the anion $(C_5H_5^-)$[11] and of cycloheptatriene to give up one electron to form the cation $(C_7H_7^+)$[12] can be explained. The HMO theory thus gave the aromatic sextet a mathematical expression. According to Huckel's theory any number of $\pi$-electrons which fitted the expression $(4n + 2)$ where n equals an integer is a closed shell whereas cyclic polyolefins which did not conform to this formula (e.g. cyclobutadiene and cyclooctatetraene) would not have the same stabilization. Huckel's Rule has also been used to explain the aromaticity of heterocyclic compounds and of inorganic compounds such as borazole (VII).[13]

The rule further predicted new non-benzenoid aromatic systems wherein the

closed shell of electrons was made up of 2, or 10 or 14 etc. (i.e.
$4n + 2$ ) $\pi$-electrons. In conformity with this rule, cyclopropenium
cation (VIII)[14], cyclobutadiene dication (IX)[15], cyclooctatetraenyl
dianion (X)[16] and cyclononatetraenide anion (XI)[17] have been brought
to light more recently.
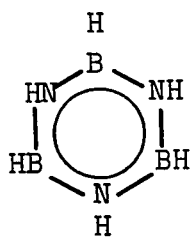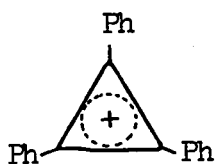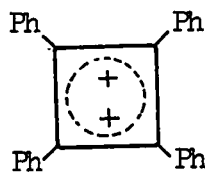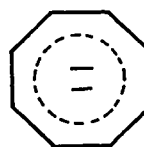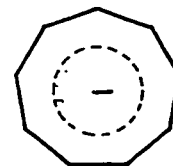


|     |      |     |     |     |
|-----|------|-----|-----|-----|
| VII | VIII | IX  | X   | XI  |

Another challenge, which the Huckel theory had posed to the
synthetic organic chemist, is its implication that there should exist
a host of non-benzenoid aromatic systems beginning with 10 $\pi$-electrons
(and conforming to the $(4n + 2)$ rule), has been met recently by
Sondheimer and co-workers[4] with the synthesis and characterization of the
so-called "annulenes". The name "annulenes" has been given to monocyclic
hydrocarbons consisting of alternate single and double bonds. The
analogous compounds in which one or more of the double bonds have been
replaced by triple bonds are termed "dehydro-annulenes". Some examples
of these systems are shown in formulas XII to XVI.

These groups of compounds are expected to be aromatic provided
they contain a reasonably coplanar carbon skeleton and contain $(4n + 2)$
out-of-plane $\pi$-electrons. Alternate members of the annulene series
have $(4n + 2)$ $\pi$-electrons. But in medium sized rings the overcrowding of
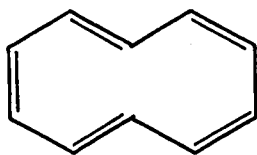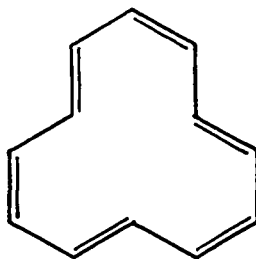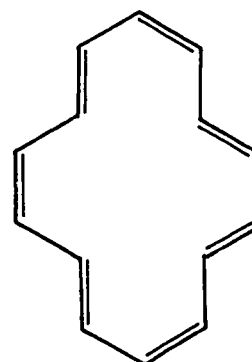
XII XIII XIV
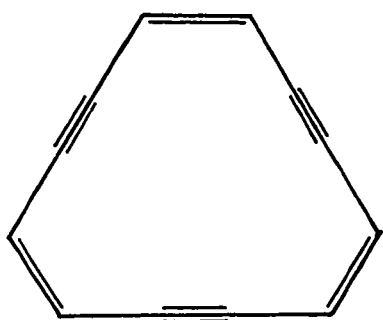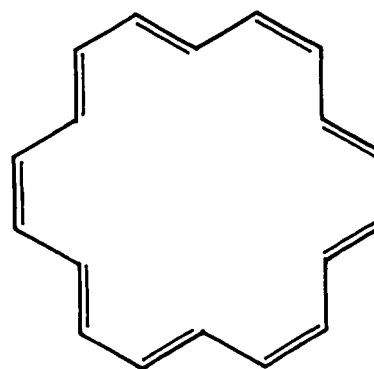
XVI XV

hydrogen atoms in the center of the rings might prevent a planar arrangement of the carbon skeleton.[19] However, [18]-annulene is found to be aromatic in the sense that it has a high stabilization energy (106 ± 6 kcal/mole as measured from heat of combustion), has a planar symmetrical structure as determined by X-ray studies (which showed a center of symmetry and hence ruled out bond alternation), and has $\pi$-electron delocalization as shown by its nmr spectrum[18].

It seems that the Huckel Rule has its limitations when one gets to larger rings. Recent calculations by Dewar and Gleicher[20] not only show strikingly that there is an alternation in resonance energies (between the $4n$ and $(4n + 2)$ $\pi$-electron systems, all annulenes of the

4n type having negative resonance energies), but also that [26]-annulene and [30]-annulene are predicted to be non-aromatic and to be at variance with the Huckel Rule. The results are illustrated in Table I and Fig. 2. Fig. 2 provides a clear explanation for the cut-off in aromaticity in

Table I. $\pi$-Binding Energies and Resonance Energies of Annulenes

| Annulene | $E_{\pi b}$ (e.v) | $E_R$ (e.v.) |
|---|---|---|
| Cyclobutadiene | 3.091 | - 0.815 |
| Benzene | 7.177 | 1.318 |
| Cyclooctatetraene | 7.485 | - 0.327 |
| [10]-Annulene | 10.844 | 1.079 |
| [12]-Annulene | 11.667 | - 0.051 |
| [14]-Annulene | 14.294 | 0.623 |
| [16]-Annulene | 15.489 | - 0.135 |
| [18]-Annulene | 17.854 | 0.277 |
| [20]-Annulene | 19.215 | - 0.315 |
| [22]-Annulene | 21.573 | 0.090 |
| [24]-Annulene | 22.901 | - 0.535 |
| [26]-Annulene | 25.160 | - 0.229 |
| [28]-Annulene | 26.977 | - 0.365 |
| [30]-Annulene | 28.824 | - 0.471 |

(4n + 2) $\pi$-electron systems, first suggested by Longuet-Higgins and Salem[21].

From the foregoing discussions, it can be seen that a short precise definition of aromaticity is rather difficult. Various definitions of aromaticity and aromatic character have appeared recently, among them are those by Baker[22], Dewar[23], Lloyd[24], Vol'pin[6], to mention a few. The most recent one is that due to Badger: "An unsaturated cyclic or polycyclic molecule or ion (or part of a molecule or ion) may be classified as aromatic if all the annular atoms participate in a conjugated system such that, in the ground state, all the $\pi$-electrons (which are derived from atomic orbitals having axial orientation to the ring) are accommodated in bonding molecular orbitals in a closed

(annular) shell"[25].
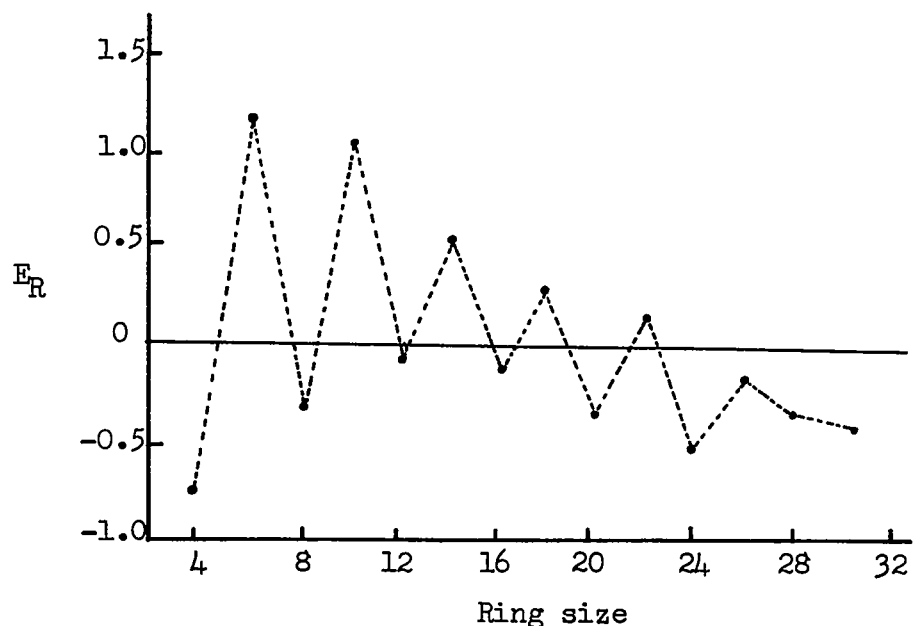


Fig 2.

As was brought out earlier, a definition of aromaticity or aromatic character based on the criteria of chemical reactivity or stability is inherently unsound. The value of the so-called resonance energy of the system as a criterion for aromaticity is also doubtful because low chemical reactivity is only accidentally connected with the resonance energy. It has been pointed out that the total stabilization represented by the thermochemical data (i.e. the resonance energy) is not solely due to delocalization of $\pi$-electrons[26].

The other, apparently better, criteria that have been recently employed in assessing aromaticity (i.e. a quantitative measure of the property) are based on the measurement of physical properties which can be accounted for in terms of $\pi$-electron delocalization. One of these

involves the examination of the nmr spectrum of the compound with respect to the chemical shifts of the protons attached to the cyclic system. The applied magnetic field causes induced circulation of the delocalized π-electrons and consequently ring currents are set up in the molecule. The ring currents are believed to be responsible for the deshielding of the protons attached to the outside of the aromatic rings contributing to the observed chemical shifts of these protons. Thus the chemical shift has been considered as a quantitative measure of the ring current and consequently an aromatic compound may be defined in this sense as one which will sustain a ring current. The magnitude of this current is a function of the delocalization of the π-electrons in the system and therefore a measure of the aromatic character[27,28]. The <u>degree</u> of aromaticity could thus apparently be measured relative to benzene in accordance with the chemical shift difference. This criterion has been applied to the annulenes[18].

However, recent studies[29-33] seem to indicate that while possession of a ring current is a sensitive test to aromatic character, caution must be exercised in using this (and the chemical shift) as a quantitative measure of aromaticity. There has also been some doubt as to the origin of the diamagnetic anisotropy possessed by a cyclic conjugated system such as benzene. According to Musher[34] delocalization of the π-electrons plays little part in accounting for the anisotropic magnetic susceptibility (and chemical shift) and that it is unreasonable to define aromaticity in terms of the ability to sustain a ring current. Musher's explanation has also been criticized[35].

Another approach to a quantitative criterion of aromaticity involves the phenomenon of diamagnetic susceptibility exaltation. Dauben

and his coworkers[36] have developed a new, empirical, experimental criterion for aromaticity in cyclic polyenic hydrocarbons. According to them the diamagnetic susceptibility exaltation, defined as the difference between the measured molar susceptibility and the susceptibility estimated neglecting the contribution of ring current, is a property solely of aromatic compounds. Nonbenzenoid _aromatic_ compounds exhibit exaltation, pseudoaromatic compounds (i.e., compounds possessing fully conjugated peripheries but none of the electronic characteristics of aromatic compounds) do not. The exaltation is found to be proportional to the theoretically calculated "London diamagnetism" of aromatic compounds.

It must be pointed out, however, that all the compounds studied by Dauben et al. are hydrocarbons, most of which were neutral molecules possessing little or no dipolar character. The application of the diamagnetic susceptibility exaltation as a quantitative criterion of aromaticity has also been criticized on the grounds of uncertainties in the values used for the diamagnetic constants for the atoms and bonds, of the need to use "constitutive corrections", and especially of the uncertainties in the origin of the susceptibility (which is closely associated with the problem of the ring current).

As matters stand at present, an all-embracing definition of aromaticity or a quantitative criterion for it is difficult, if not impossible. If aromatic character is to be considered in terms of ground state properties, it would seem that the molecular orbital definition (e.g. ref. 25) would be the most favorable one, at least as a qualitative one. The question of aromaticity is still a riddle, and will, to say the least, continue to fascinate the physical-organic chemist. It is not surprising therefore that research in this field

continues with vigour.

In keeping with the molecular orbital requirements and the Huckel Rule, the qualitative definition of aromaticity can be met by five-membered carbocyclic systems in which all ring atoms are conjugated and have six $\pi$-electrons in the ring. The cyclopentadienide anion is often cited as being aromatic in this sense. The negatively charged cyclopentadienide ring may occur not only as a discrete anion but also as part of a dipolar molecule as in the various cyclopentadienylides (e.g. XVII B) and the fulvenes. The cyclopentadienylides are considered as examples of non-benzenoid aromatic compounds, and in resonance language, can be considered as receiving contributions from an extreme zwitterionic form XVII B and a covalent form XVII A.



|       |       |       |
|-------|-------|-------|
| A     | XVII  | B     |

where $G^+$ in XVII B is:-

(a)[37]: $-\overset{+}{N_2}$          (b)[38]: $-\overset{+}{N}(CH_3)_3$          (c)[39]: $-\overset{+}{P}Ph_3$

(d)[40]:           (e)[41]:           (f)[42]: $-N=N-\overset{+}{P}Ph_3$

(g)[43]: 
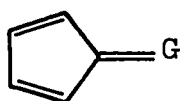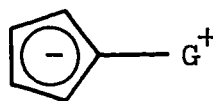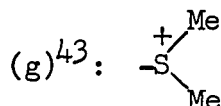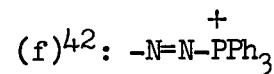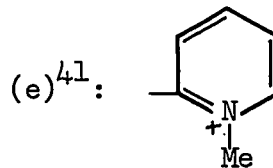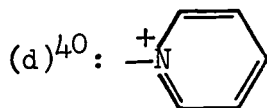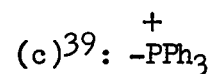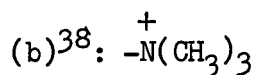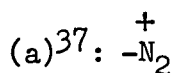
Compounds XVII (a) - (g) are some representative examples of the cyclopentadienylides. (Only forms of the type XVII B can contribute to XVII (a), XVII (b) and XVII (d)). Most of these ylides have large dipole moments in accordance with the dipolar nature of the molecule. The chemistry of these ylides have been little explored. Based on chemical reactivity only XVII (c) can be construed as aromatic in the sense of benzene and its derivatives. It was shown to couple with benzene diazonium chloride[42]. The pyridinium ylide is unstable in air and is readily hydrogenated[40]; the diazo compound XVII (a) is thermally unstable, decomposes on standing and is also readily hydrogenated[44]. Little is known about the trimethylammonium cyclopentadieneylide (XVII (b)) and the other ylides.

In view of the theoretical significance of these ylides and of the availability of only meager chemical data pertaining to these compounds, it seemed of interest and importance to study some of the aspects of the chemistry of these compounds.

# STATEMENT OF THE PROBLEM

The present study was initiated to examine some aspects of the "non-benzenoid aromaticity" of the cyclopentadiene moiety in various cyclopentadienylides of the type:
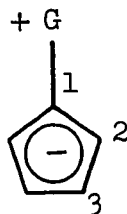


In view of the published reports, that some of these ylides undergo electrophilic substitutions in the five-membered ring in the 2- and/or 3-positions, it was decided to investigate various electrophilic reactions and especially to determine the site(s) of protonation in these ylides and their derivatives.

It was also decided to investigate the possibility of dipolar cycloadditions of suitable reagents to these ylides. Of no less interest was also the investigation of the hitherto unestablished mechanism of formation of several of these ylides by way of the 1,4-additions of bromine to cyclopentadiene and subsequent reactions with appropriate reagents.

# DISCUSSION

## General:

Despite the more than 30 years of strong interest and study in the nature and limits of aromaticity, disagreement persists over the best definition of aromaticity. A satisfactory theoretical description of the phenomenon has been developed[45] and various experimental criteria for its presence have come to be accepted. Difficulties seem to arise because quantities amenable to theoretical calculation cannot be easily experimentally determined, and *vice versa*.

## Physical Aspects of Aromaticity:

The requirements for the modern electronic definition of aromaticity can be met by five-membered ring compounds in which all ring atoms are conjugated and six $\pi$-electrons are available in the ring. The cyclopentadienide ion falls in this category, and its aromaticity accounts for the existence and stability of many cyclopentadiene derivatives containing an electron-donating exocyclic atom or group. Among such cyclopentadiene derivatives are the well known fulvenes (XVIII) and the various ylids derived from cyclopentadiene (XVII). While many fulvenes have been shown to have substantial thermochemical resonance energies, the nmr parameters[46] and the chemical properties[47] characterize these compounds as diene-like rather than aromatic.



XVIII

16
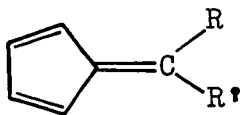
Most of the ylids (XVII) are considered to belong to the nonbenzenoid aromatic class of compounds. As was pointed out earlier, aromaticity can be assessed by various approaches which do not necessarily arrive at the same conclusion. The evaluation of the importance of the dipolar resonance contributors to the ground states of these ylids and their derivatives is necessary for understanding these systems and to assess any $\pi$-electron delocalization energy they might possess. Such an evaluation is severely limited due to lack of a universally accepted criterion for $\pi$-electron delocalization.

Use of chemical reactivity (or lack thereof) as a criterion for evaluating aromaticity is not on firm grounds because chemical reactivity is a broad spectrum with no clear-cut demarcations which separate the aromatic from the nonaromatic. The same goes for the use of data related to diamagnetic susceptibility, nmr ring currents, or other physical properties dependent on $\pi$-electron delocalization. Although limitations of these approaches are now fairly widely recognized, there have been attempts, even while the present study was in progress, to correlate the aromaticity with nmr parameters in cyclopentadienides of the type XVII.[48,49]

Nmr and MO Criteria:

Smith and coworkers[48] have investigated the nmr spectra of several cyclopentadienides. The $\pi$-bond orders of the five-membered ring have also been calculated. They have found that the bond orders (p) and vicinal coupling constants (J) followed a linear relationship from which it was possible to draw inferences regarding the aromaticity of these systems. The J-p relationship has already been shown to exist in a series of six-membered aromatics[50]. The degree to which the ylids meet the electronic criteria of aromatic compounds can be inferred from bond

orders. It has been suggested by Streitwieser[51] that in $\pi$-systems
single bonds will have $p < 0.4$, aromatic compounds will have
$p = 0.5 - 0.7$, and that double bonds are characterized by $p > 0.8$.

It has been reported[48] that the nmr spectrum of the
cyclopentadienylidene ring in the triphenylphosphonium, pyridinium and
the trimethylammonium ylids was, in each case, that of an AA'BB' system.
In the latter two ylids the upfield half of the spectrum was broadened
due to coupling with the nitrogen. The spectrum of diazocyclopentadiene
was completely symmetrical with no broadening and it closely approximated
an AA'XX' case. The spectrum of triphenylphosphoniumcyclopentadienylide
in deutereochloroform was a perturbed AA'BB' spectrum owing to coupling
with phosphorus. The phosphorus-decoupled spectrum was simpler and
$J_{HP}$'s were found to be 3.6 Hz to the proton in the 3-position of the five-
membered ring and 5.6 Hz to the proton in the 2-position, from a computer
analysis of the spectrum.[52] The spectral parameters and bond orders
are summarized in Table II and the J-p relation is shown in Fig. 3.

No MO calculations for the triphenylphosphonium ylid and
diazocyclopentadiene were carried out in the study cited[48], due to lack
of parameters for the exocyclic groups, and the p values for these two
systems were calculated from the J-p relationship. However one HMO
calculation for the triphenylphosphonium ylid has subsequently been
published by other workers[53] and it is interesting to note that the p
values reported are $p^{2,3}$, $p^{3,4} = 0.718$ and $0.590$ which are close to the
values computed by Smith and coworkers.[48] Either calculation indicates
substantial aromatic character for the phosphorus ylid and some dienoid
character for diazocyclopentadiene.

It appears reasonable that nmr coupling constants are related to

Table II. Nmr Data[48] for Some Cyclopentadienides
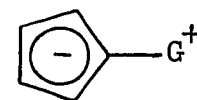
| Cyclopentadienides | $\tau$ | Coupling Constants(Hz) | | | | Bond Orders | |
|---|---|---|---|---|---|---|---|
| | | $J_{2,3}$ | $J_{3,4}$ | $J_{2,4}$ | $J_{2,5}$ | $p^{2,3}$ | $p^{3,4}$ |
| Triphenylphosphonium | 3.64 | 3.84 | 2.80 | 1.89 | 2.16 | 0.705[≠] | 0.559[≠] |
| Pyridinium | 4.12 | 4.19 | 2.34 | 1.50 | 2.18 | 0.752 | 0.540 |
| Trimethylammonium | 5.44 | 3.84 | 2.96 | 2.26 | 1.74 | 0.762 | 0.516 |
| Diazo | 3.67 | 4.93 | 2.70 | 1.87 | 2.20 | 0.858[≠] | 0.545[≠] |
| Dimethylfulvene | 3.70 | 5.45 | 2.40 | 1.50 | 2.40 | 0.828 | 0.444 |
| Diphenylfulvene | 3.70 | 5.17 | 2.21 | 1.38 | 1.94 | 0.814 | 0.460 |

≠ Calculated from the J-p relation, all other p values from
MO calculations.
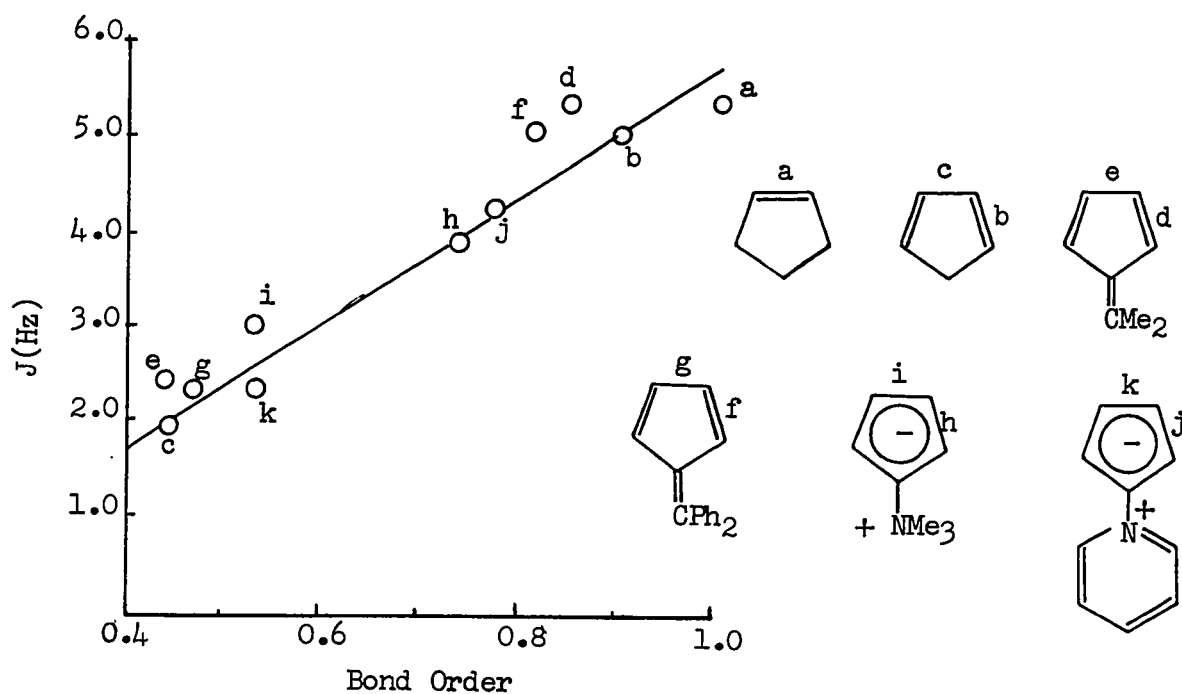


Fig 3.

$\pi$-electron delocalization in that both are related to bond order. For a qualitative estimation of the $\pi$-electron delocalization in the cyclopentadienylidene system in the ylids and their derivatives, one might compare the coupling constants of the protons in this ring to those in cyclopentadiene. The analogous coupling constants in cyclopentadiene are $J_{2,3}$ = 5.06 Hz and $J_{3,4}$ = 1.94 Hz[54]. Assuming that in a completely delocalized five-membered ring the coupling constants would converge to an average of 3.5 Hz[49], the cyclopentadienylidene ring in these compounds indicate some enhancement of $\pi$-electron delocalization.

In his valence bond treatment of the spin-coupling phenomenon, Karplus[55] has shown that vicinal coupling constants decrease linearly with increasing length of the intervening carbon-carbon bond, provided the internal bond angles and hybridization remain constant. Since the relation of bond order to bond length is essentially linear, the observed linear behavior of the J-p relation is not surprising. The Karplus treatment also predicts a decrease in J of ca 60% in going from a true double bond to a single bond, which is in fair agreement with the experimental observation. Thus the variation of J with bond length might be considered the more fundamental relation. However, the importance of the J-p plot stems from the bond order - bond length correlation and is useful in calculating bond orders for many compounds where no bond length measurements have been carried out.

As was pointed out earlier, there are a number of objections to using the proton chemical shifts as a criterion for assessing aromaticity in the cyclopentadienylidene ring in the ylids and their derivatives. Considerations such as the influence of solvent polarity, the change in charge densities on the ring carbons introduced by the

exocyclic group, and the magnetic anisotropy of the exocyclic group rule against the applicability of the chemical shifts in any attempt to assess the aromaticity in these compounds.

## Chemical Aspects of Aromaticity:

In the chemical sense aromatic compounds are characterized by "reduced unsaturation and the tendency to retain type", as illustrated, for example, by their tendency to undergo substitution rather than addition reactions. It was decided to explore this angle in connection with the aromatic character of the cyclopentadienides. The present study, from the outset, was directed towards finding answers to the following questions: (i) Would the cyclopentadienylidene ring in the ylids undergo electrophilic substitution without disruption of the exocyclic groups? (ii) Which position is the most subject to substitution? (iii) How reactive is the ring system compared to other aromatic systems? (iv) Could the ylids be induced to undergo cycloaddition reactions? (v) Which position(s) in the five-membered ring will be protonated?

## Electrophilic Reactions:

There have already appeared in the literature reports regarding electrophilic substitution reactions in triphenylphosphoniumcyclopentadienylide[42] and in diazocyclopentadiene[56]. In the case of the phosphonium ylid, the aromatic character of the cyclopentadienylidene ring was demonstrated by its coupling reaction with phenyldiazonium chloride and p-nitrophenyldiazonium chloride. That the coupling took place at the 2-position has been established by the following sequence of reactions:
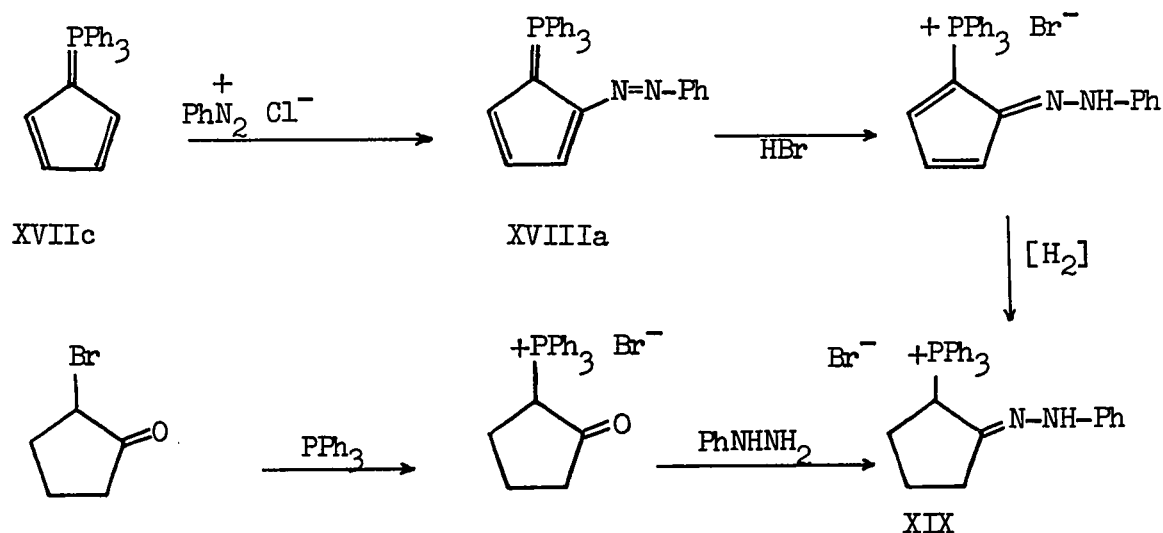
The same phenylhydrazone (XIX) was obtained from both series of reactions, thus establishing the structure of the product of coupling of the ylid with phenyldiazonium chloride. No product, resulting from the coupling at the 3-position was obtained.

In the case of diazocyclopentadiene a more systematic study of the electrophilic substitution reaction has been carried out[52]. This ylid underwent five electrophilic substitution reactions without destruction of the ylid $\pi$-electron system. Nitration gave a mixture of the 2- and 3- nitrodiazocyclopentadienes in a ratio of 2:1. Both isomers have been isolated and characterized by their nmr spectra. Treatment of diazocyclopentadiene with phenyldiazonium tetrafluoroborate gave 2-phenylazodiazocyclopentadiene (XXII). According to the authors, attempts to confirm the position of substitution in XXII through nmr analysis failed as "the phenyl group complicated and obscured the absorptions of the other hydrogens". So the structural assignment was made on the basis of analogy with the behavior of the triphenylphosphonium ylid
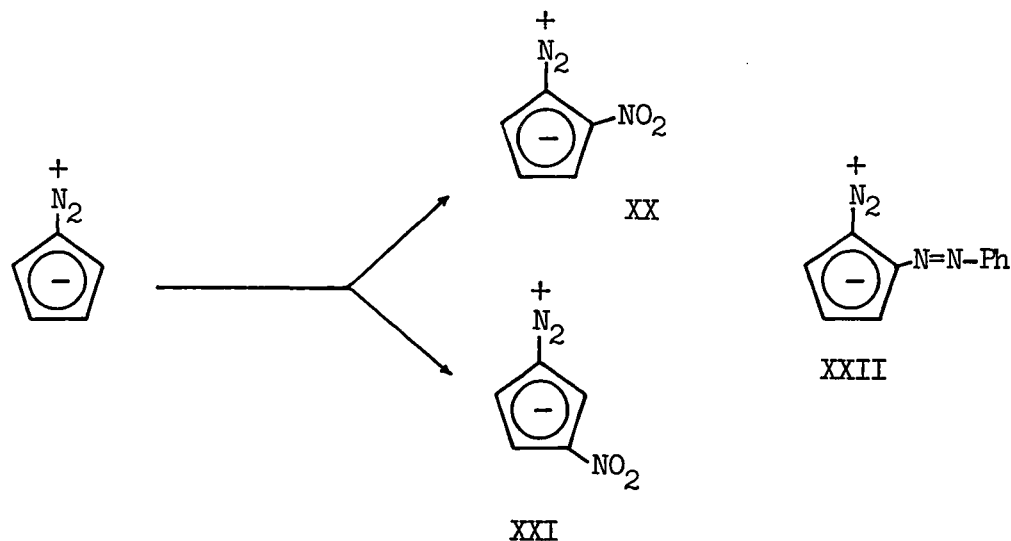
towards diazo coupling.

Bromination of diazocyclopentadiene with N-bromosuccinimide in acetonitrile gave tetrabromodiazocyclopentadiene. Mercuration resulted in the formation of a highly unstable 2,5-diiodomercuri derivative, which was readily converted to 2,5-diiododiazocyclopentadiene. Diazocyclopentadiene also added 1,2 to tetracyanoethylene to give an unstable acid, which readily lost the elements of hydrogen cyanide to produce 2-(tricyanoethylene)diazocyclopentadiene XXIII. The position
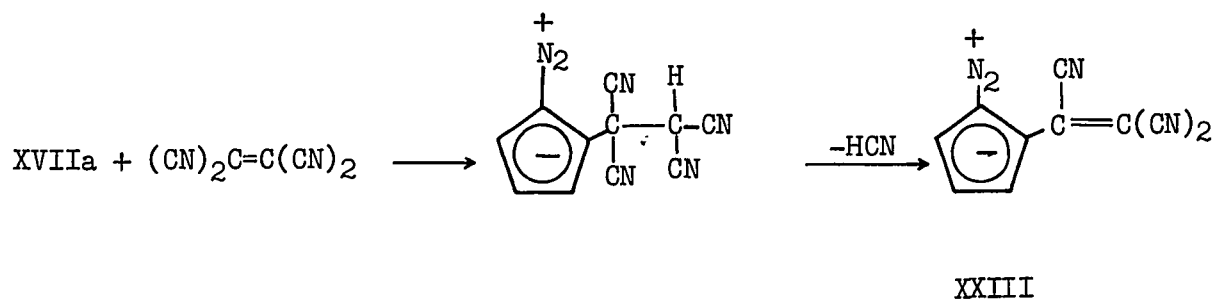


of substitution was demonstrated by the nmr spectrum of XXIII which was very similar to that of XX.

The reactions discussed in the foregoing sections indicate a preference for electrophilic attack on the 2,5-positions over the

3,4-positions of diazocyclopentadiene. The authors speculate the reason for this in the following way. The reactions probably involve cations as intermediates, which serve as models for the rate-determining transition states as shown below.
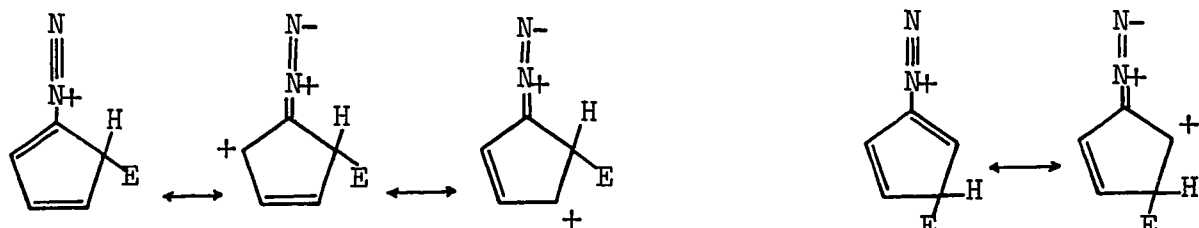
The cation that corresponds to substitution at the 2,5-positions is "through conjugated" and has three important contributors to the resonance hybrid. The cation which reflects substitution at the 3,4-positions is "cross conjugated" and has only two important contributors to the hybrid. Thus the transition state for the 2,5-positions should be the more stable, as is observed.

In contrast to the behavior of tetracyanoethylene, dimethylacetylene dicarboxylate adds 1,4 to the diazocyclopentadiene to give a maroon solid which was assigned the structure XXIV.

XXIV
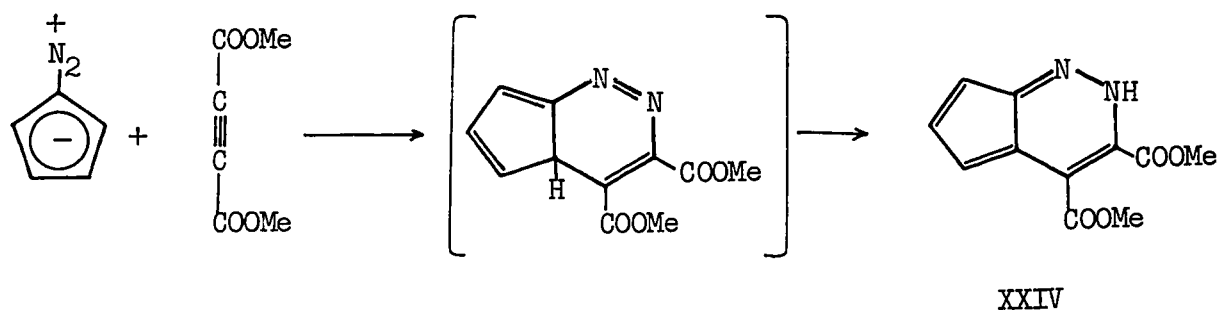
While the present study was in progress a communication

appeared regarding the reaction of triphenylphosphoniumcyclopentadienylide[57].

Equimolar quantities of the phosphonium ylid and tetracyanoethylene,

when mixed in methylenechloride in the presence of triethylamine,

gave a quantitative yield of (1,2,2-tricyanovinylcyclopentadienylidene)-

phosphorane XXVI. An equimolar mixture of the ylid and tetracyanoethylene

XXV

a    XXVII    b

XXIX          XXVI          XXVIII
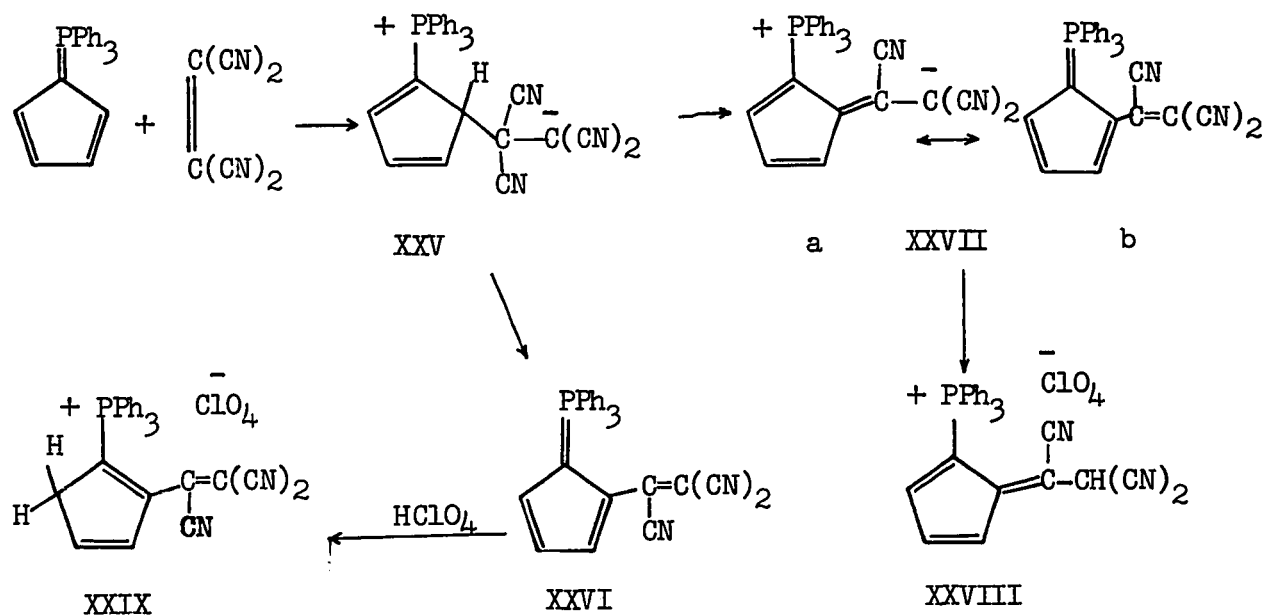
in methylene chloride, in the absence of the base, gave a different

product which was unstable. This compound was assigned the structure

XXVII by the authors on the basis of ir and uv data, and was considered

to be the geometrical isomer of XXVI. It was stated that no

satisfactory elemental analysis could be obtained for this compound.

However, the authors claim to have isolated a stable perchlorate of

this unstable isomer and on the basis of ir and uv data the perchlorate

was assigned the structure XXVIII. They were unable to isolate a

stable perchlorate for the stable isomer; however, this unstable

perchlorate had a different uv spectrum and was assumed to have the structure XXIX.

If the tricyanovinyl derivative of the phosphorus ylid is capable of existing in two different geometrical forms, then it is difficult to understand the reason why one of the forms is stable and the other so unstable that it could not be isolated. It is also difficult, a priori, to estimate the energy barrier for the rotation around the C - C bond between the C-2 carbon of the cyclopentadienylidene ring and the carbon atom of the tricyanovinyl group. Whatever this barrier is, it must be a consequence of a significant contribution from dipolar 'resonance forms' such as XXVIIa. In this connection it is interesting to note that Cram and Partos[56] have not considered the possibility of two different geometrical isomers in the case of the 2-(tricyanovinyl)-diazocyclopentadiene (XXIII).

Reactions of Triphenylphosphoniumcyclopentadienylide:

In the present study 1:1 addition products between the triphenyl phosphonium ylid and phenylisocyanate, phenylisothiocyanate, or dimethyl-acetylene dicarboxylate have been isolated and characterized. Refluxing a 1:1 mixture of the ylid and phenylisocyanate in benzene afforded a brownish yellow crystalline solid after removal of the solvent. Purification by either column chromatography over alumina or repeated crystallizations from chloroform - methanol gave a white crystalline solid. This solid (as well as the other 1:1 adducts) was found to retain chloroform tenaciously after crystallizations as shown by the nmr spectra in DMSO solutions, and therefore prolonged drying in vacuo at elevated temperatures was necessary to obtain an analytically pure sample.
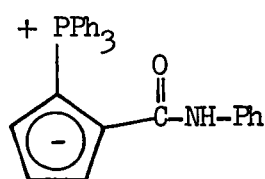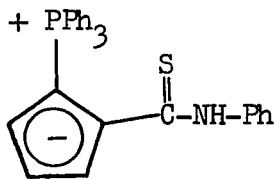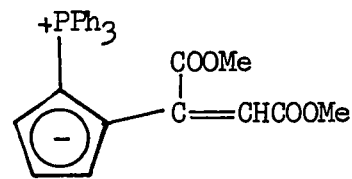
XXX                    XXXI                    XXXII

The nmr spectrum of the phenylisocyanate derivative was

consistent with its formulation as the N-phenyl amide XXX. Isocyanates

have been known to react with many phosphorus ylids, the products

depending on the structure of the ylid[58]. Trippett and Walker[59]

reported a novel acylation of ylids by phenylisocyanate. Reaction of

the latter with carbethoxymethylenetriphenylphosphorane gave the

amido-ester XXXIIIa. Methylenetriphenylphosphorane could be doubly



XXXIIIa
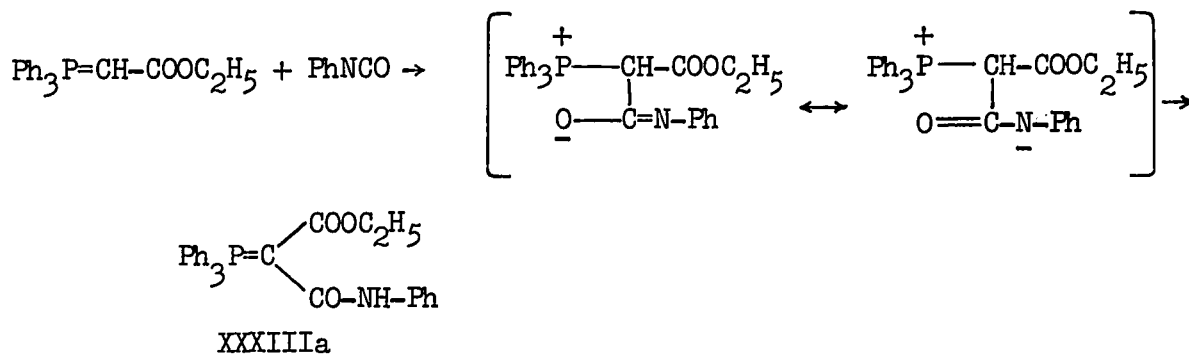
acylated with the same reagent, indicating the reactivity of both the

hydrogen atoms $\alpha$ - to the phosphorus atom. These reactions are believed

to proceed by initial addition to the carbonyl group of the isocyanate as

for a typical Wittig reaction followed by a proton transfer directly to

the nitrogen or via the enol form. In the reaction indicated above

the intermediate betaine was a sufficiently strong base to carry out the

generation of the acylated ylid. In those instances where there was

no hydrogen on the carbon atom adjacent to the phosphorus, a normal

Wittig reaction resulted producing a ketenimine and triphenylphosphine

oxide[60,61].

The reaction of ylids carrying $\alpha$-hydrogen atoms giving 1:1

and 1:2 addition products with isocyanates is not limited to phosphorus

ylids. Recently it has been shown[62,63] that dimethylsulfoxoniummethylide

also reacts with isocyanates where both $\alpha$-hydrogens are successively

used up in the acylation.

$$
\underset{\text{Me}}{\overset{\text{Me}}{>}}\overset{O}{\underset{}{S}}=CH_2 \quad \xrightarrow{\text{RNCO}} \quad \underset{\text{Me}}{\overset{\text{Me}}{>}}\overset{O}{\underset{}{S}}=CH-\overset{O}{\underset{}{C}}-NH-R \quad \xrightarrow{\text{RNCO}} \quad R-NH-CO-\underset{\underset{\text{Me}\quad\text{Me}}{S\rightarrow O}}{\overset{}{C}}-CO-NH-R
$$
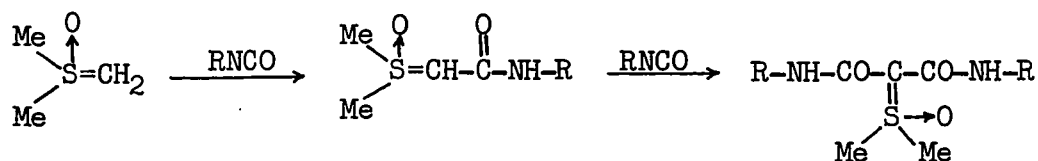
In the case of triphenylphosphonium cyclopentadienylide there

is no hydrogen atom on the carbon adjacent to the phosphorus atom.

However, the present study suggests that no Wittig reaction took place,

as shown by the absence of any triphenylphosphine oxide in the

product. Besides, the material balance indicated that the product is

a 1:1 adduct. The product had the characteristic N-H frequency in the

ir spectrum at 3400 cm$^{-1}$, and a typical amide carbonyl absorption at

1630 cm$^{-1}$ (Ir spectrum No. 2). The nmr spectrum in DMSO (Nmr spectrum

No. 6) revealed the N-H absorption at $\delta$ 9.1; when CDCl$_3$ was used as the

solvent, the nmr spectrum did not show clearly the peak due to N-H proton.

The uv spectrum (EtOH) of the product had $\lambda_{max}$ at 325 nm ($\epsilon$ = 30,800).

The reaction giving rise to the product XXX shows that a $\beta$-hydrogen atom

of this phosphorus ylid is reactive towards phenylisocyanate. No such

acylations involving β-hydrogens of ylids seem to have been brought
to light so far.

The reactions and reactivities of isocyanates can be best
understood by considering the electronic structure of the isocyanate
group. A qualitative consideration of the "resonance structures" from
the standpoint of molecular orbital theory indicates that the electron
or charge density is greatest on the oxygen (highest net negative
charge) and least on the carbon (highest net positive charge), the
nitrogen atom being intermediate with a net negative charge[64]. The
reaction at the 2-position of the ylid can be envisaged as shown below:
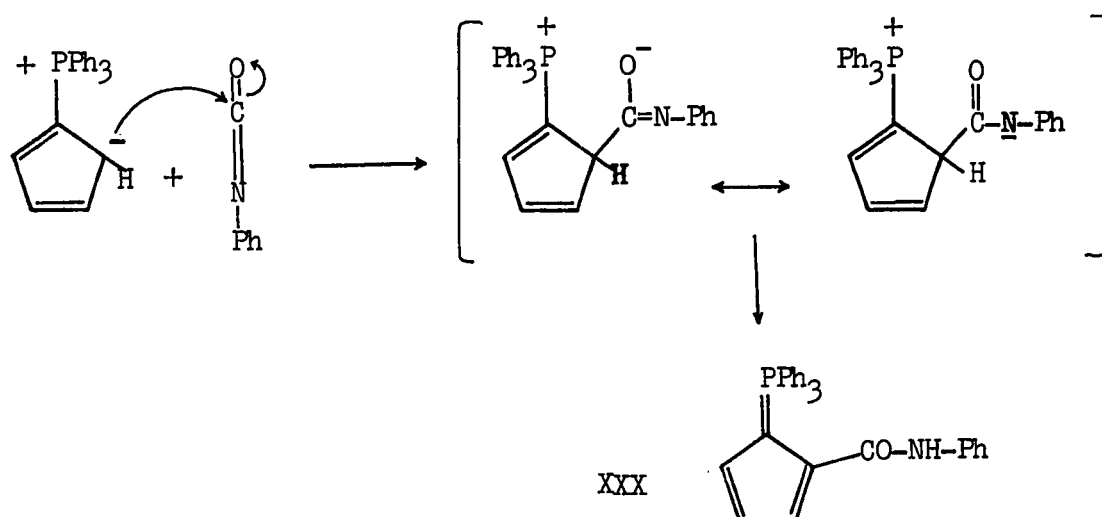


It is interesting to note that no product corresponding to
the double acylation (making use of both the β-hydrogens in the ylid)
could be obtained either by treating the ylid with 2 molar equivalents
of phenylisocyanate or by treating the product XXX with an addition
molar equivalent of phenylisocyanate. This result would seem to indicate
that only one of the two symmetrically placed β-hydrogen atoms of the ylid
is available for reaction with phenylisocyanate. This would mean that

once the mono addition product is formed, the electron density (and therefore the nucleophilic character) at the other β-carbon of the five-membered ring would be decreased. Electrophilic attack on this carbon would thus be much less efficient. This is not surprising since the amide substituent attached to the previously electron-rich five-membered ring is electron withdrawing, thereby decreasing the electron density on the five-membered ring compared to that in the free ylid.

The reaction of phenylisothiocyanate with triphenylphosphonium-cyclopentadienylide was analogous to that of phenylisocyanate. Only the 1:1 addition product could be obtained. This product is assigned the thioamide structure XXXI on the basis of its ir (Ir Spectrum No. 3), uv (Uv Spectrum No. 2), and nmr (Nmr Spectrum No. 8) spectra.

There have been a limited number of studies involving the reactions of phosphorus ylid with conjugated alkynes[65]. Hendrickson[66] had reported that phenacylidenetriphenylphosphorane reacts with dimethyl acetylenedicarboxylate to give a 1:1 adduct which was assigned the cyclic oxaphosphorabenzene structure XXXIII. However, the experimental

$$Ph-CO-CH=PPh_3 \quad + \quad \begin{matrix} Y \\ | \\ C \\ \| \\ C \\ | \\ Y \end{matrix} \quad \longrightarrow$$

(Y = COOMe)

XXXIII

XXXIV

XXXV

XXXVI
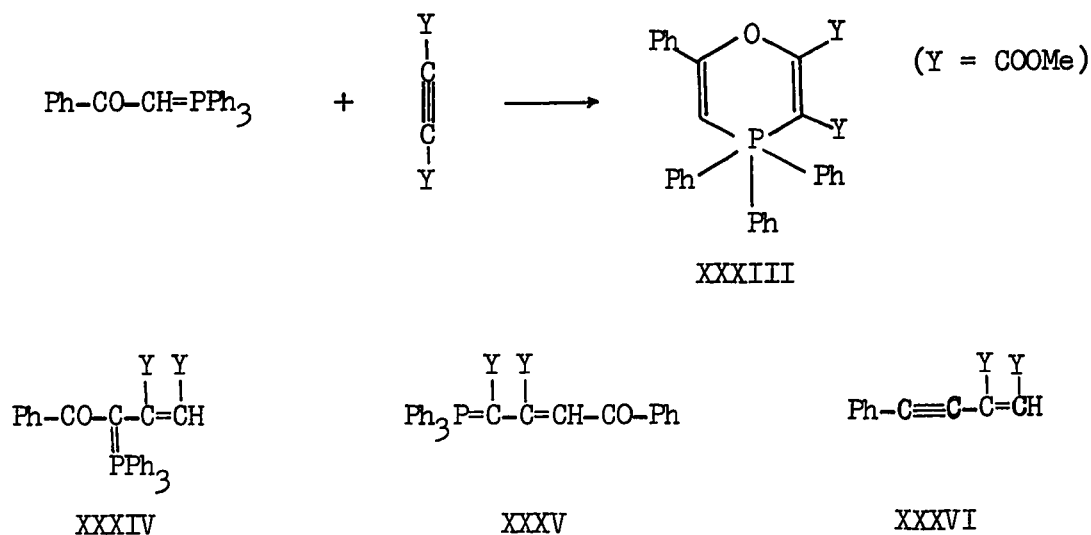
data are also in agreement with the more likely ylid structure XXXIV.
The nmr data are consistent with the latter formulation and such $\beta$-keto
ylids are known to undergo pyrolytic elimination of triphenylphosphine
oxide to yield alkynes[59]. Hendrickson's adduct did undergo such an
elimination to afford a diester (probably XXXVI), which could be
hydrolyzed and reduced (3 moles of $H_2$) to $\beta$-phenylethylsuccinic acid.
The ylid formulation XXXIV is in accord with other additions of ylids
to conjugated carbonyl compounds, i.e., a normal Michael addition followed
by a prototropic shift. Hendrickson et al.[67], in a recent paper have made
no comment about the originally proposed cyclic structure XXXIII, but
have reported (without experimental data) that the ylid XXXIV is formed
in methanolic solution and the rearranged ylid XXXV is formed in
ethereal solution.

Trippett[68] has investigated the reaction of
cyanomethylenetriphenylphosphorane with dimethylacetylene dicarboxylate.
The product of the reaction is believed to be a new ylid XXXVI, presumably
via a prototropic shift in the intermediate. However, no concrete
evidence was provided for the structure.

$$Ph_3P=CHCN + Y-C\equiv C-Y \rightarrow \left[ \overset{+}{Ph_3}P-\overset{\overset{CN}{|}}{CH}-\overset{\overset{Y}{|}}{C}=\overset{\overset{Y}{|}}{C^-} \right] \rightarrow Ph_3P=C\begin{smallmatrix} \diagup CN \\ \diagdown \underset{\underset{Y}{|}}{C}=CHY \end{smallmatrix}$$

XXXVI
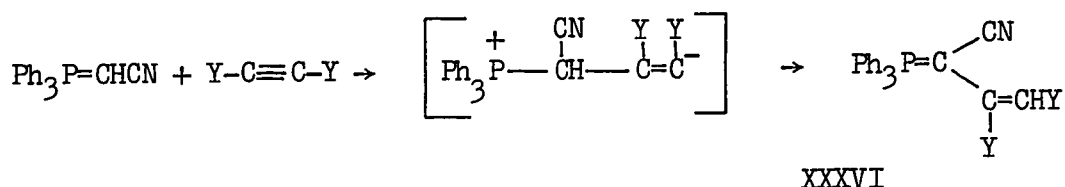
When the ylid undergoing a Michael addition to an acetylenic
ester does not have any $\alpha$-hydrogen another course of reaction seems to
prevail, as was shown by Brown et al[69]. Benzhydrylidenetriphenylphosphorane

added to dimethylacetylenedicarboxylate to form a new ylid XXXVIII. The

structure of this product has not been established unambiguously, but

Bestmann and Rothe[70] have discovered analogous reactions between the

ester and ylids of the type RR'C=PPh$_3$ where R and R' were a variety of

alkyl groups. These authors have established the structure of the

products to be analogous to XXXVIII.
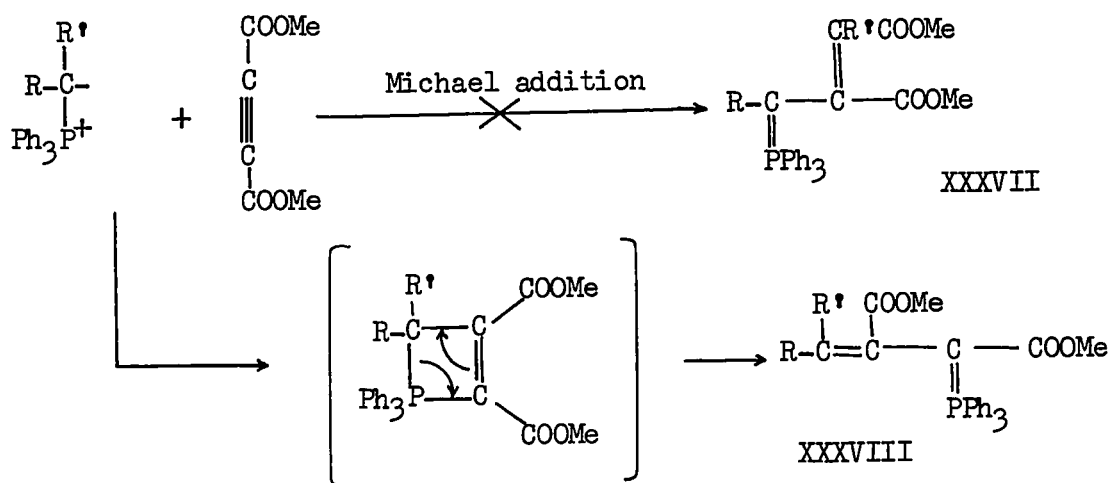


It would appear reasonable to assume that the initial step in

all these reactions with acetylenic diesters was the addition of the

ylid to the alkyne in a Michael type addition to form the intermediate

carbanion XXXIX (Y = COOR). If both R and R' are other than hydrogens
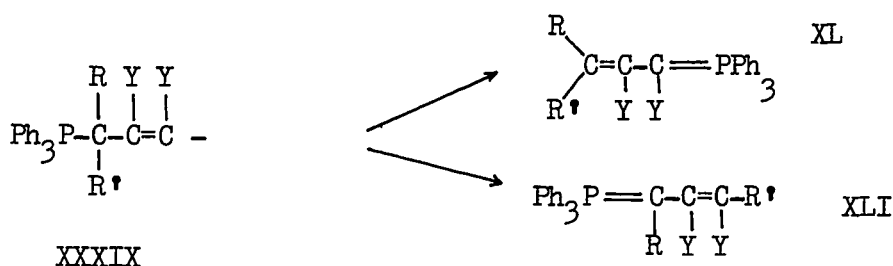


and are not prone to migrate the only course open to the intermediate

would be the formation of a four-membered intermediate or transition state

which will rearrange to a new ylid XL. However, if R or R' is a hydrogen, or

a group capable of providing some degree of stabilization for a

potential ylid, the intermediate could complete the Michael type reaction to form the ylid XLI.

In the present study triphenylphosphoniumcyclopentadienylide and the acetylenic ester gave spontaneously a 1:1 adduct, which on purification and crystallization afforded a yellow crystalline solid. The ir spectrum of the compound showed the ester carbonyl absorptions at 1730 cm$^{-1}$ and 1695 cm$^{-1}$. The uv spectrum in EtOH had a $\lambda_{max}$ at 390 nm ($\epsilon$ = 74,000). The nmr spectrum in CDCl$_3$ exhibits two sharp peaks of equal area (3 protons each) at $\delta$ 3.3 and $\delta$ 3.0. There is a sharp one proton singlet at $\delta$ 4.7. Further downfield the spectrum exhibits three complex multiplets of equal area centered around $\delta$ 6.00, $\delta$ 6.25 and $\delta$ 6.75 (one proton each), followed by a complex 15-proton multiplet (Nmr spectrum No. 10). The material was found to retain chloroform from which it was crystallized as was shown by the nmr spectra in DMSO of samples not meticulously dried in vacuo for prolonged periods. In DMSO the chloroform absorption appears around $\delta$ 8.3.

As in the reactions with phenylisocyanate and phenylisothio-cyanate, attempts to obtain a 1:2 adduct either by treating the ylid with 2 moles of dimethylacetylenedicarboxylate or by treating the 1:1 adduct with a further one mole of the ester were unsuccessful, the only product isolated in each case being the 1:1 adduct. Under similar conditions the ylid failed to react with conjugated acetylenic ketones of the type R-C≡C-CO-R' (R = Ph; R' = CH$_3$).

The following three posibilities have to be considered for the structure of the 1:1 adduct:
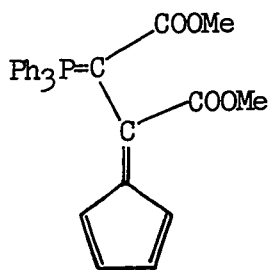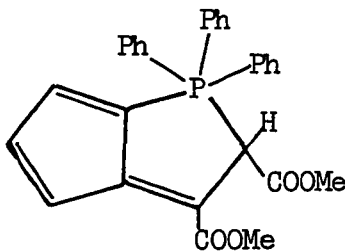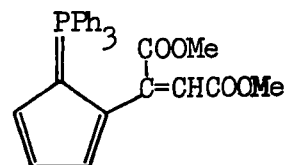
XLII                    XLIII                    XLIV

Considering the fact that the phosphonium ylid has no α-hydrogens and
in view of the reports[67,69] that ylids with no α-hydrogens react with the
acetylenic ester to give a rearranged ylid one would be tempted to
choose structure XLII. However, the presence of a one-proton singlet
at δ 4.7 in the nmr spectrum would appear to rule out this
possibility. Structure XLIII has a tertiary hydrogen on a carbon
carrying a carbomethoxy group. Since a phosphorus atom is also bonded
to this same tertiary carbon, one would expect a splitting of the
hydrogen resonance due to coupling with phosphorus. As this splitting
is not evident, structure XLIII is also ruled out. The ir, uv and nmr
data are consistent with the structure XLIV.

In the aromatic region of the nmr spectrum, the three complex
multiplets of equal area are assigned to the hydrogen atoms of the five-
membered ring in XLIV. The positions of these peaks and their splitting
patterns are very similar to those in the 1:1 adducts of the ylid with
phenylisocyanate, phenylisothiocyanate and the coupling product with
benzenediazonium chloride. The one-proton singlet at δ 4.7 is assigned
to the vinylic proton on the exocyclic group and the two 3-proton
singlets to the methyl groups in the carbomethoxy groups. At this stage

it is rather difficult to make unequivocal assignments for the two

methyl resonances. Also, little can be said at present regarding the

configuration (i.e., cis or trans) of the exocyclic group. In view

of the claim[57] that two geometrical isomers were observed for a similar

addition product of the ylid with tricyanovinyl chloride and

tetracyanoethylene, one would expect the existence of four possible

isomers (one pair when the ester groups are cis, and another pair when

they are trans). The mp, uv, nmr and ir data indicate that the product

is a single isomer. It would seem that the most likely configuration

for the exocyclic group is with the two ester groups trans to each other.

Further work, including some variable temperature nmr study, is indicated

for the unambiguous establishment of the structure.

Spectral Data:

A summary of the uv data and the proton resonance spectra

(of the five-membered ring) for the various mono-substituted

triphenylphosphoniumcyclopentadienylides is given in Table III. The

aromatic region of the nmr spectra of all the following derivatives

are very similar, including the splitting patterns of the resonances

of the protons in the five-membered ring. In all cases absorptions due

to two protons in the cyclopentadienylidene ring appear upfield with

good resolution. In the diazoderivative and the phenylisothiocyanate

adduct, and to some extent in the phenylisocyanate adduct, the

absorption due to the third hydrogen is obscured by the peaks due to

the phenyl hydrogens. Assignments of the 3 one-proton complex

multiplets to the three protons of the five-membered ring is rather

difficult as the shielding properties of the triphenylphosphonium group

and the groups represented by G are not easy to assess. However,

Table III. Spectral Data for
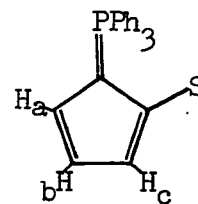


| | | Nmr ($\delta$-values of ring protons) | Uv (EtOH) $\lambda_{max}$, nm. ($\epsilon$) |
|---|---|---|---|
| Substituents S | $-N=N-Ph$ | $H_a(H_c)$: 5.9 (2q) <br> $H_b$ : 6.4 (2t) <br> $H_c(H_a)$:* | 219 (42,900) <br> 255 (13,700) <br> 455 (20,600) |
| | $-\overset{O}{\overset{\|}{C}}-NH-Ph$ | $H_a(H_c)$: 5.9 (m) <br> $H_b$ : 6.3 (2t) <br> $H_c(H_a)$: 7.0 (m) | 325 (30,800) |
| | $-\overset{S}{\overset{\|}{C}}-NH-Ph$ | $H_a(H_c)$: 6.0 <br> $H_b$ : 6.3 (2t) <br> $H_c(H_a)$: * | 323 (24,200) <br> 380 (26,200) |
| | $-\overset{COOMe}{\overset{\|}{C}}=CHCOOMe$ | $H_a(H_c)$: 5.9 (2q) <br> $H_b$ : 6.3 (2t) <br> $H_c(H_a)$: 6.7 | 390 (74,000) |

t = triplet; q = quartet; m = multiplet; * = unresolved

tentative assignments are made as shown in Table III on the basis of analogy with the report of Carm and Partos[56] for other but similar 1,2-disubstituted cyclopentadienides.

The proton $H_b$ has the most symmetrical environment, being placed between $H_a$ and $H_c$. This is expected to produce a triplet. However, this proton is also coupled to the phosphorus[48] which would

further split this signal, and indeed the spectrum recorded at a 50 Hz

sweep width of this region clearly indicates two overlapping triplets.

The positive character of the phosphorus atom would deshield the proton

$H_a$ and shift its signal to lower field (lowest of the 3 protons in the

five-membered ring). This would be a quartet due to coupling to $H_b$ and

$H_c$, but coupling to the phosphorus[48] would make it two quartets.

Similarly $H_c$ appears as a pair of quartets. Indeed each of the two

absorptions ($H_a$ and $H_c$) appears as a pair of overlapping quartets.

For $H_c$ (the one appearing at the highest field of the three protons),

the lower field peak of one quartet and the higher field peak of the

other appear at the same place, so that this absorption appears as a

group of seven peaks with the middle peak having a higher intensity.

Attempted Reactions:

There has been a report regarding the action of carbon disulfide

on phosphonium ylids[71]. Fluorenylidenetriphenylphosphorane has been

found to react with carbon disulfide at room temperature, or at the

boiling point of $CS_2$, to yield XLV. The 2,4-dimethylene-1,3-dithiabutane

derivative (XLV) is believed to arise from an unstable thioketene

derived from LXVa which dimerizes to the final product.

In the present study the reaction of carbon disulfide with

triphenylphosphoniumcyclopentadienylide has been tried under various

conditions. At room temperature no reaction was observed to take place

either with or without the presence of solvents. Upon refluxing in

carbon disulfide alone, or in the presence of solvents such as benzene,

the ylid seemed to react producing an orange-yellow amorphous solid

XLVa                    XLV
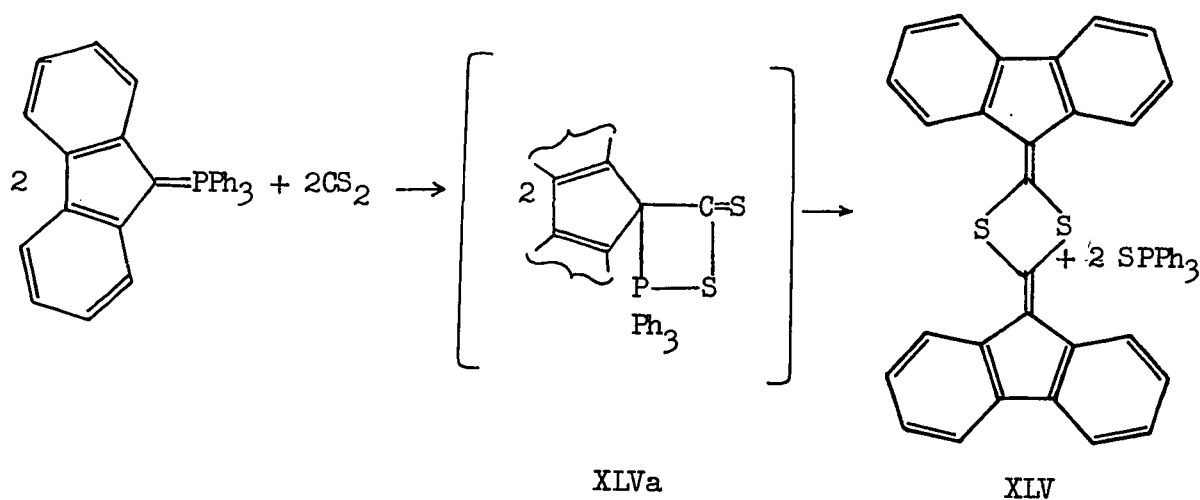
with an odor reminiscent of thiol derivatives. However, the product
could not be crystallized from a variety of solvents and mixed solvents.
It was partially soluble in aqueous potassium hydroxide solution.
The ir spectrum of the solid was not specially informative as was the
nmr spectrum. At this stage it is not possible to state whether the
reaction between $CS_2$ and the ylid produces one or more of the following
types of compounds:



XLVI                XLVII                XLVIII
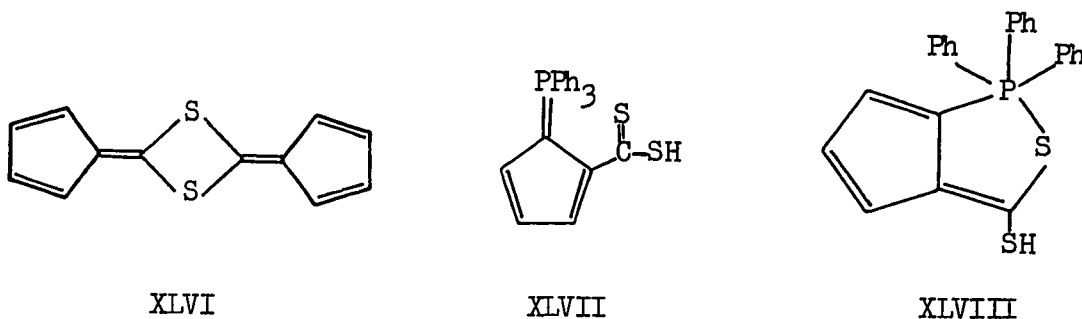
Compounds of the structure XLVII and XLVIII are not expected to be
stable in the monomeric form and would probably undergo decomposition
or polymerization under the reaction conditions used. Further study of
this reaction under more carefully controlled conditions is indicated.

A reaction of triphenylphosphoniumcyclopentadienylide and

benzonitrile oxide was attempted under various conditions. The products isolated were varying amounts of unreacted ylid and benzofuroxan, the dimer of the nitrile oxide. The reaction was always accompanied by the production of much tarry material. While the present study was nearing completion a communication appeared in the literature[72] where the reaction between cyclopropylidenetriphenylphosphorane and benzonitrile oxide has been described. The cycloaddition product XLIX was reported to have been produced in 61% yield. In the present study it was hoped



XLIX
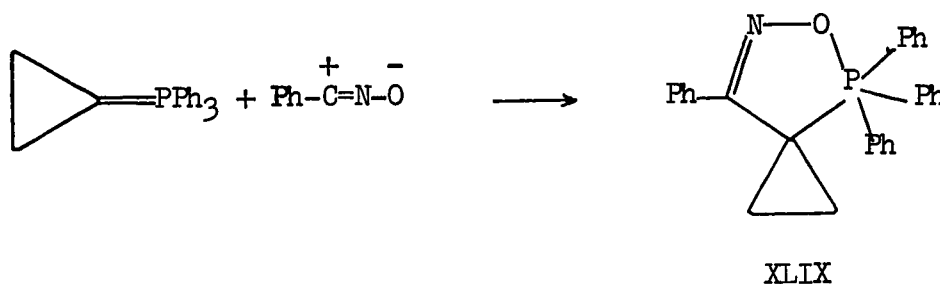
that a derivative of the structure L would be produced, assuming the



L                           LI
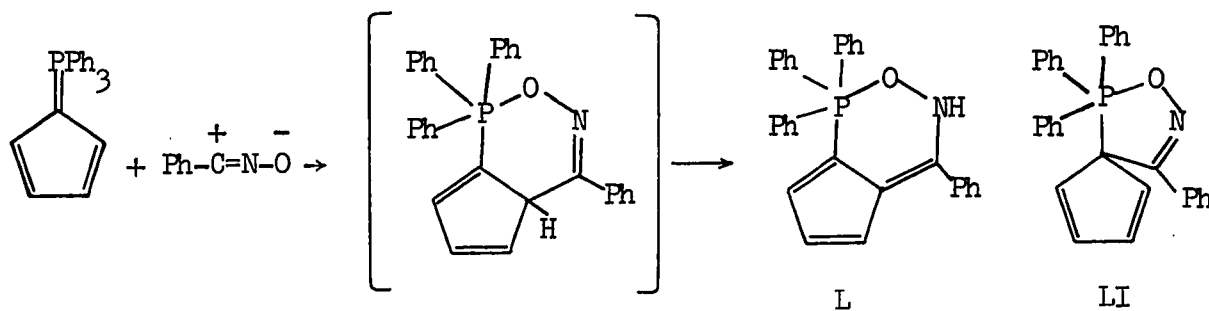
preferred site of electrophilic attack on the cyclopentadienylidene ring is the 2-position. A derivative of the structure LI is not expected to be stable and most likely will undergo polymerization or decomposition.

Some phosphorus ylids have been found to react with benzyne,

the products being triphenylphosphine derivatives[73]. The reaction is
pictured as proceeding via a dipolar intermediate (produced as a 1:1
adduct of benzyne and the ylid) which then rearranges to the product.
In the present study it was hoped that 2-phenyltriphenylphosphoniumcyclo-
pentadienylide (LII) would be produced by the reaction of benzyne with
the ylid. However, this project had to be abandoned, due to repeated
explosions during the experimental procedure.

Reactions of the ylid with cycloheptatrienone (tropone) and
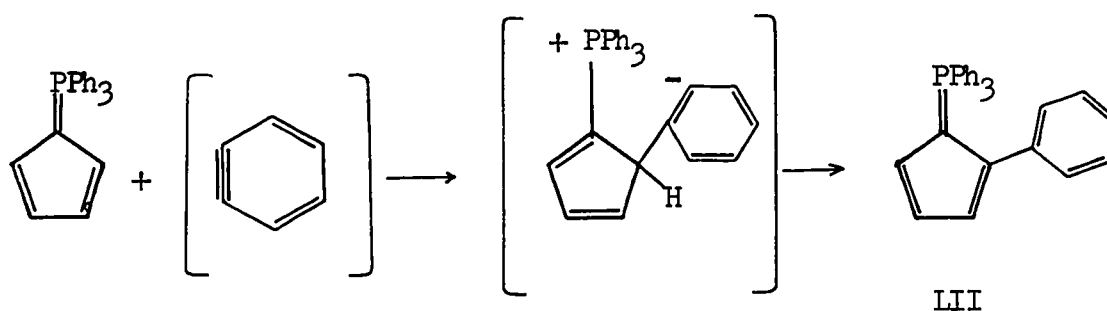


diphenylcyclopropenone were attempted under various conditions. But
only varying amounts of the starting materials could be identified as
products in these reactions. Although it is well established that the
ylid itself or the ketones themselves are unreactive in normal Wittig
reactions it was of interest to see if the ylid will react with the
ketones under forcing conditions to yield the calicene derivative LIII



a                    b

LIII

a          LIV          b
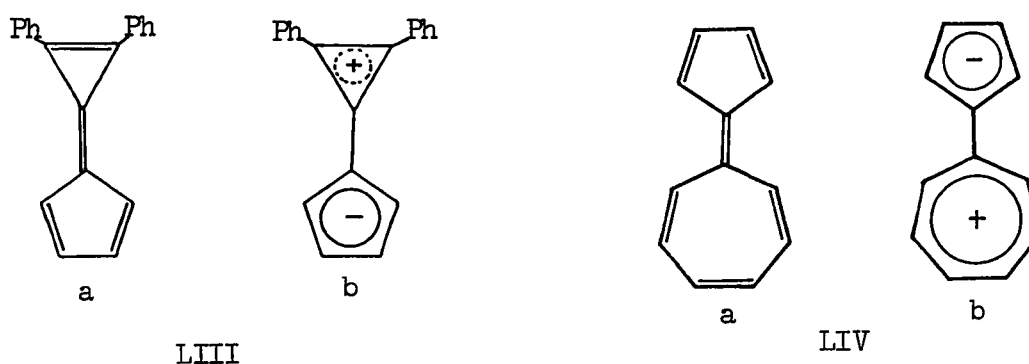
and sesquifulvalene LIV. In each system the two rings can accommodate the charges as shown in the structures a and b, and each ring will conform to the Huckel $(4n + 2)$ $\pi$-electron rule. Hence the two systems would be expected to exhibit some stability. No such products could be identified under the conditions employed for these reactions.

All the reactions that have been tried with triphenylphosphonium-cyclopentadienylide have been tried with pyridinium, picolinium, cyclopentadienylides, (cyclopentadienylhydrazono)triphenylphosphorane and trimethylammoniumcyclopentadienylide(XVIIf); however, attempts to isolate any stable product, under a variety of conditions, failed in all cases. The pyridinium and picolinium ylids are not as stable as the hydrazono ylid, and decompose on exposure to air and light. Reactions with various reagents produced only tarry materials.

Attempted Reactions on other Cyclopentadienylides:

The attempted reactions of the hydrazono ylid are worthy of some comment. In general, it was noted that this ylid was more reactive than triphenylphosphoniumcyclopentadienylide, and rapidly gave rise to resinous materials and intractable tars. In the reaction with phenyliso-cyanate small quantitics of triphenylphosphine oxide could be isolated as the only identifiable product. Similarly in the reaction with phenylisothiocyanate only trace amounts of triphenylphosphine sulfide could be isolated. These reactions indicate that, to the extent that triphenylphosphine oxide and triphenylphosphine sulfide were produced, a normal Wittig-type reaction must have taken place in each case, possibly analogous to the reaction of phosphorus ylids having no $\alpha$-hydrogens[60,61]. In view of the fact that only traces of the triphenylphosphine oxide and the sulfide are produced, it would seem that the major path of the

reaction (which produced unstable products or decomposition products) must have been something other than a Wittig-type reaction mechanism, because a Wittig-type reaction would produce the system LV. The



LV
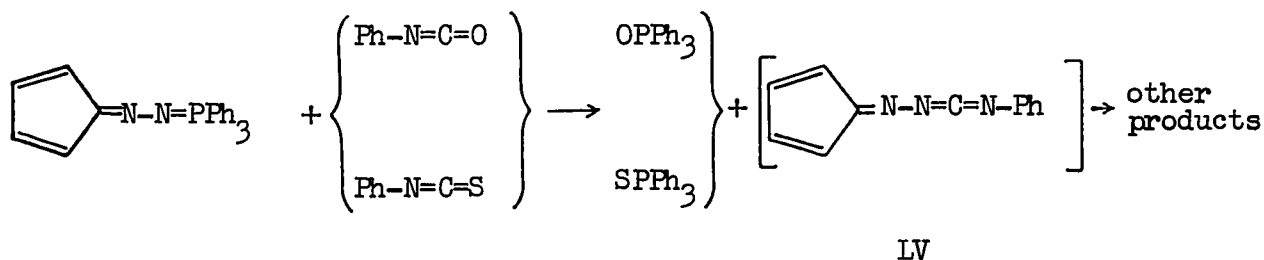
system could probably exist as a dipolar structure if a positive charge could be stabilized on the phenyl end of the system. Probably a phenyl group attached to a nitrogen atom at the end is not suited for this purpose. It was thought that para-dimethylaminobenzaldehyde would react with this ylid in a Wittig-type reaction to produce a somewhat more stable system LVI. Indeed such Wittig reactions between aldehydes and



LVI
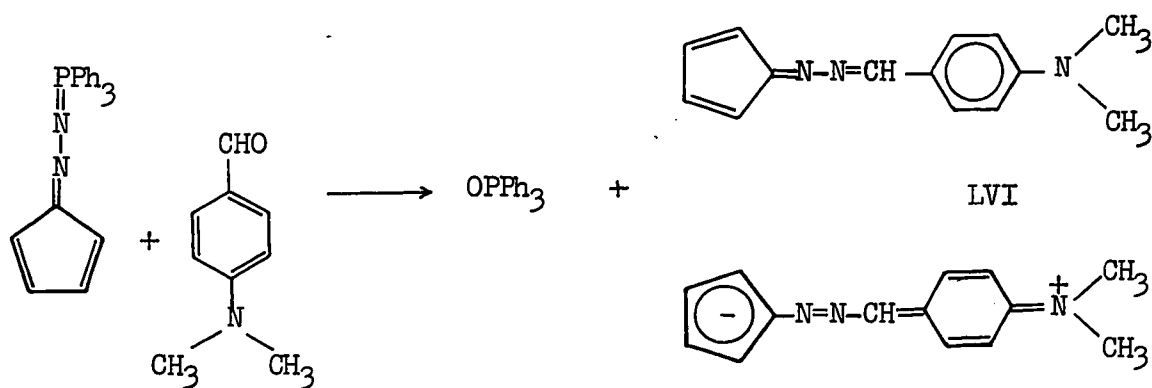
phosphinazines have already been reported[74,75]. However all attempts to effect such a reaction failed.

Reactions of this ylid with diphenylcyclopropenone and tropone

were also tried in the hope that the novel, hitherto unknown, "stable"
systems LVII and LVIII might be produced. Here too all attempts were
unsuccessful. No MO calculations on these novel systems are
available and as such any predictions about their stability on
theoretical groups would be premature.

Dimethylacetylene dicarboxylate reacted with this ylid more
readily than with triphosphoniumcyclopentadienylide, but only intractable
tars could be isolated. No product analogous to the one in the reaction
with triphenylphosphoniumcyclopentadienylide (e.g. LIX) could be
isolated. Equally unsuccessful were the attempts to obtain the 1:1
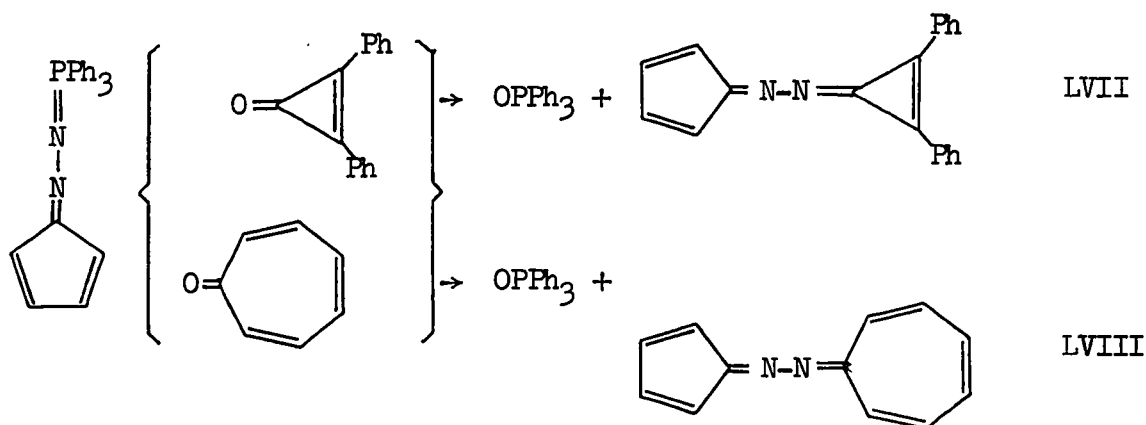
adducts LX and LXI with phenylisocyanate and phenylisothiocyanate.
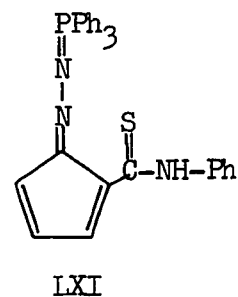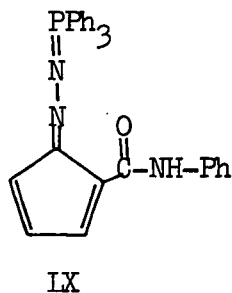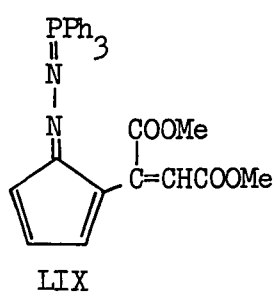
Recently it has been reported[69,76] that dimethylacetylene-
dicarboxylate reacts with iminophosphoranes (LXII) and phosphinazines
(LXIII and LXV) to produce 1:1 adducts. It is interesting to note that
the phosphinazine LXIII with an α-hydrogen atom reacted via a normal
Michael-type addition to produce a new phosphinazine LXIV, whereas
fluorenylidenetriphenylphosphinazine (LXV), which has no α-hydrogens,
reacted in a manner similar to the iminophosphorane LXII, presumably
via the phosphazacyclobutane intermediate[69]. Considering the fact that



LXII

LXIII                          LXIV

LXV                                        LXVI
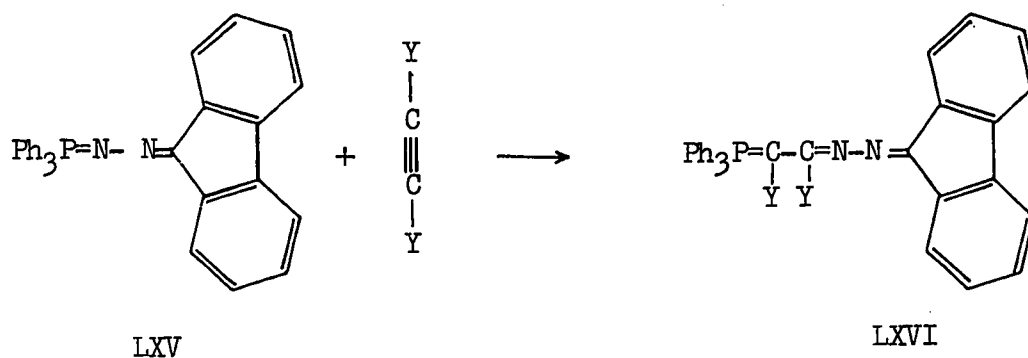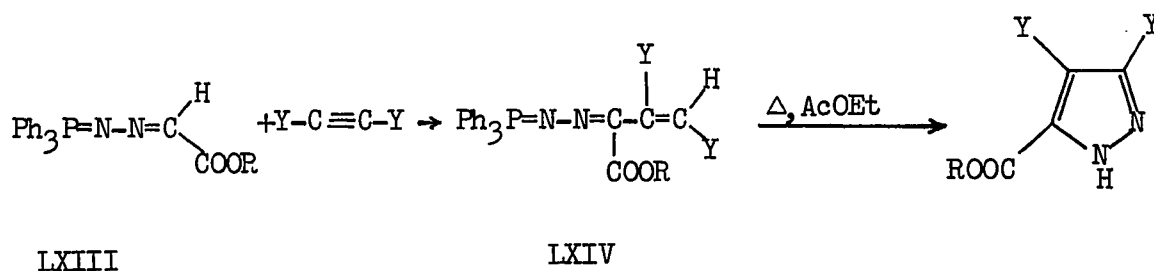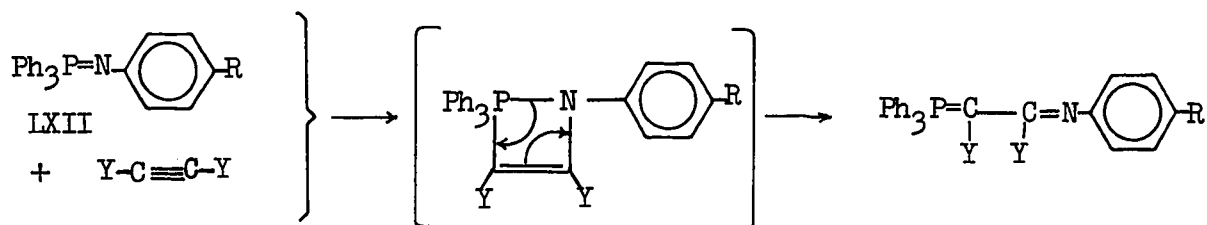
the cyclopentadienylidenephosphinazine is analogous to the fluroenylidene derivative (in that it also has no α-hydrogens), one would expect it to react with dimethylacetylene dicarboxylate to yield a phosphorus ylid of the type LXVII. However, all attempts to obtain a derivative of the type LXVII or LXVIII failed.
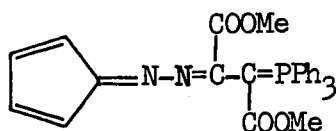


LXVII
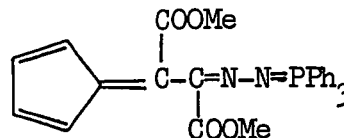
LXVIII

## Mechanisms of Ylid Formation:

One of the aims of the present study was to gain some insight into the mechanism of formation of the cyclopentadienylides prepared in the usual manner starting with cyclopentadiene. These ylids are generally prepared according to the scheme shown below:
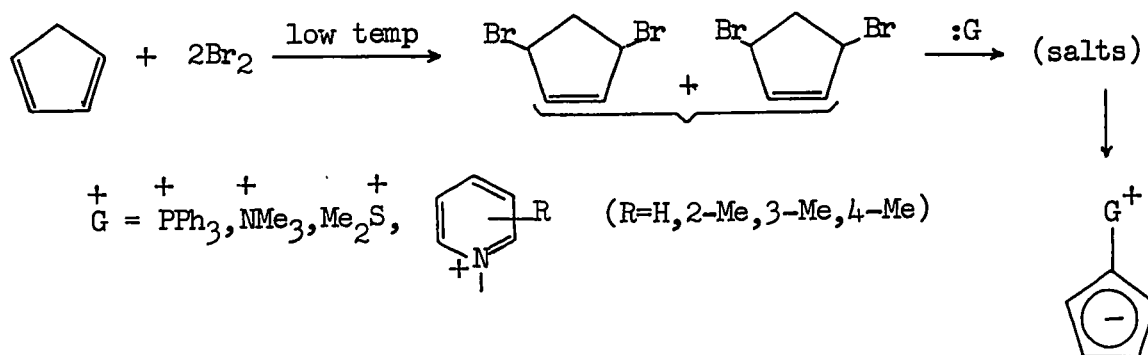


Addition of bromine to cyclopentadiene produces a mixture of cis- and trans-3,5-dibromocyclopentenes. The dibromides are then treated with two equivalents of the appropriate nucleophile G which produces the

di-'onium' salt(s). Treatment of the onium salt liberates the ylid.
To date no systematic study has been directed towards the establishment
of the structure of the "di-salt".

Cope and coworkers[77] have demonstrated that reaction of
dimethylamine with either cis- or trans-3,5-dibromocyclopentene gives
only trans-1,2-bis(dimethylamino)-3-cyclopentene LXXIII. From this it
was rationalized that the course of the reaction consisted of a normal
displacement with inversion ($S_N2$ followed by an intramolecular
displacement by an $S_N2'$ mechanism via the intermediate LXXII. LXXIII
on treatment with 2 moles of methyliodide produces the corresponding
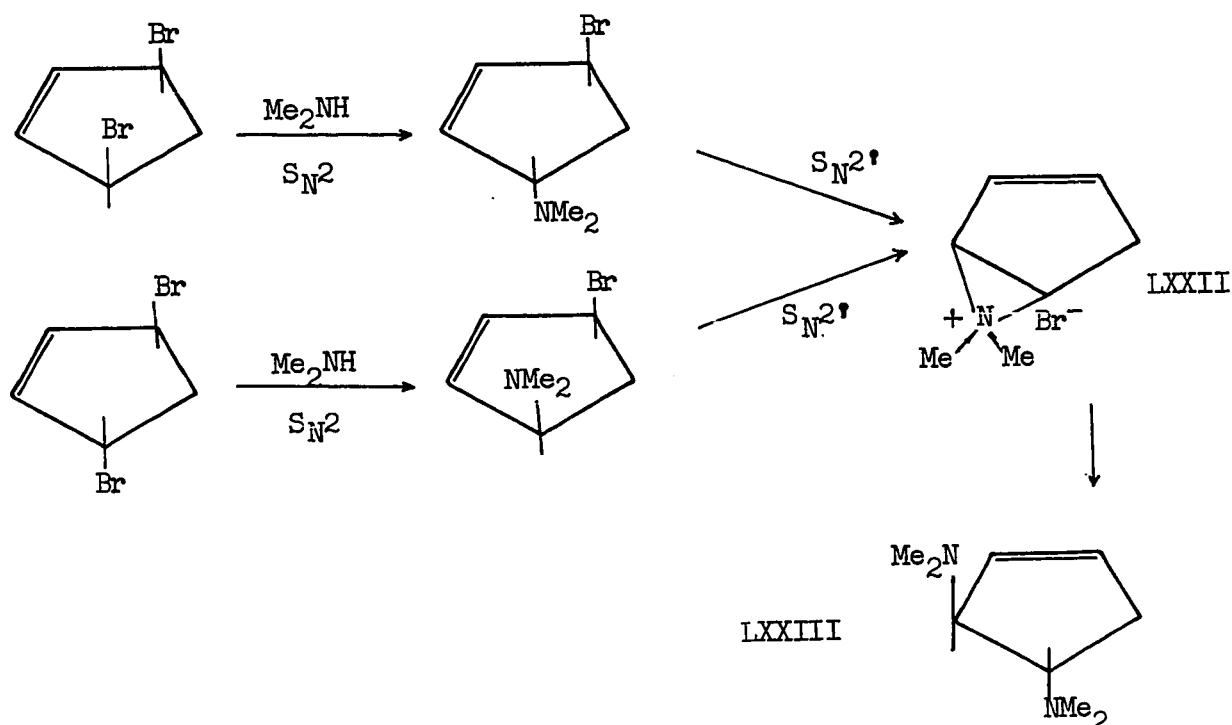


dimethiodide from which trimethylammoniumcyclopentadienylide could be
generated on treatment with aqueous potassium hydroxide[38].

Lloyd[78] has pictured the formation of pyridinium cyclopent-
adienylide (and the corresponding picolinium ylids) from 3,5-dibromo-

cyclopentene as shown below. The structures of the "di-salt" is given as LXXIV for unstated reasons. This implies that the dibromide gives the corresponding "di-salt" via a normal $S_N2$ path. However, this mechanism remains to be elucidated.



LXXIV
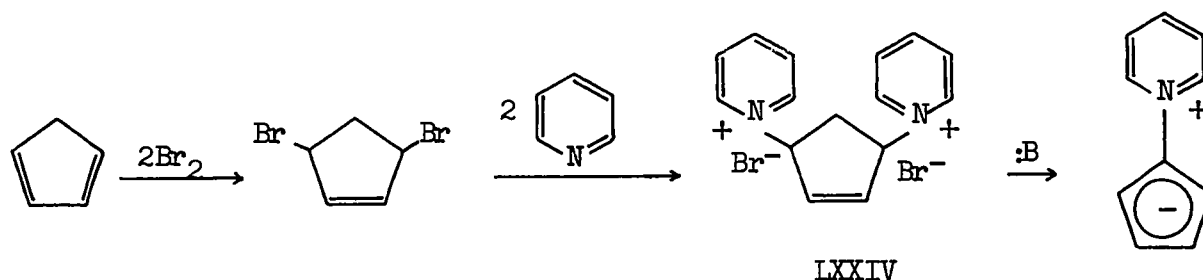
If the reaction of the nucleophile G with the 1,3-dibromo-cyclopentene follows the same general mechanism as elucidated by Cope et al.[77], the di-salt produced will be the trans-1,2-bis(dimethyl-amino)-3-cyclopentene LXXV, rather than the cis- and/or trans-3,5-cyclopentene derivatives LXXVI and LXXVII which would be formed only if normal $S_N2$ reactions took place on the dibromide. The production of



LXXV               LXXVI               LXXVII
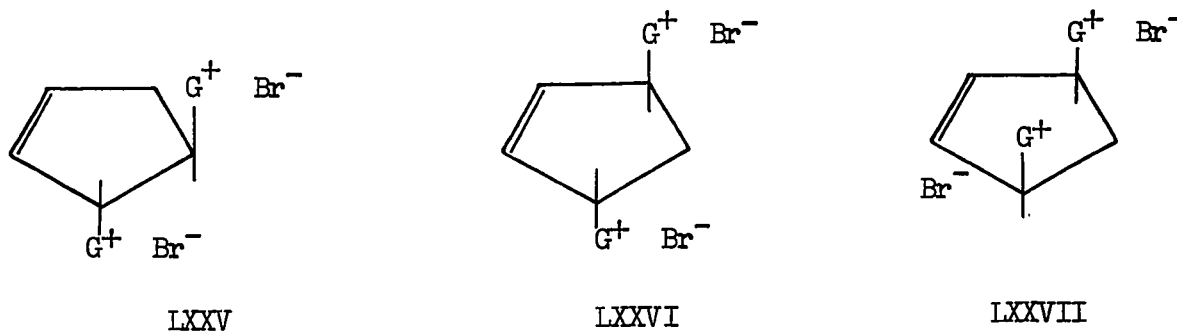
this ylid upon treatment of the salt with base can be pictured as shown below:

LXXV



cis- or trans-
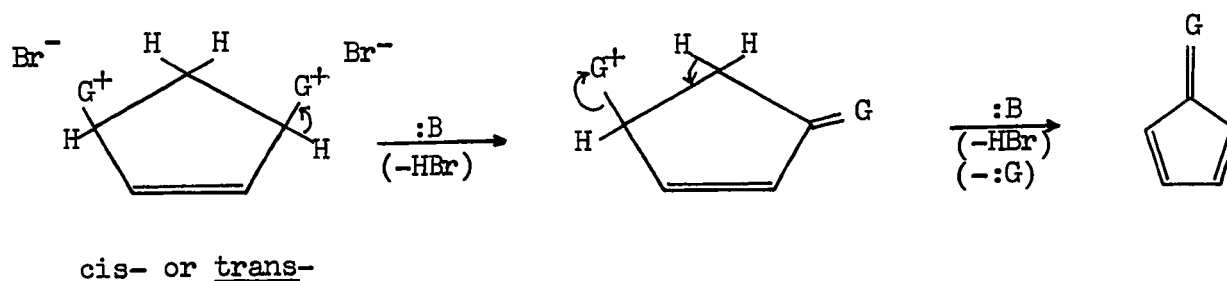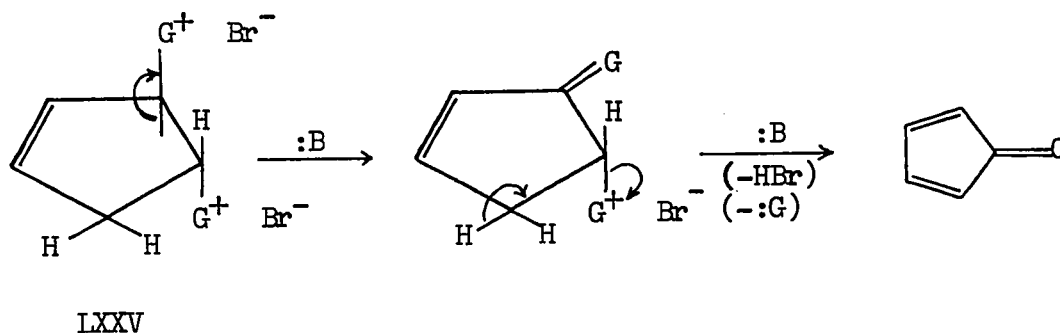
The above scheme indicates that, whatever the structure of the salt, treatment with base eliminates 2 moles of HBr and a mole of the nucleophile G. In the case of the preparation of triphenylphosphonium-cyclopentadienylide Ramirez and Levy[42] did observe triphenylphosphine as one of the reaction products.

In view of the work of Cope et al.[77], it would seem that the "di-salt", the precursor of the ylid, would be of the type LXXV. In the case of the di-phosphonium salt Ramirez and Levy[42] had suggested the possibility that the salt might have any of the three possible structures corresponding to LXXV, LXXVI and LXXVII. However, since this point is not at all clear from the available literature on cyclopentadienylides, it was decided to initiate a study to obtain information regarding the

structure of the "di-salt" in as many cases as possible.

Until recently, the "di-salt" had not been isolated in the pure form, except in the case of <u>trans-1,2</u> -bis(trimethylammonium)cyclopentene[77]. However, recently a method has been reported for the convenient isolation of the bis-pyridinium and the bis-picolinium salts which are precursors to the corresponding cyclopentadienylides[79]. These salts were prepared as described and their nmr spectra were recorded in $D_2O$ as well as in DMSO. At this stage it is rather difficult to give a complete analysis of each spectrum. They seem to be more complex than would be expected for structure such as LXXVI and LXXVII.

<u>Cis</u>-3,5-dibromocyclopentene was isolated from the products of bromination of cyclopentadiene. It was thought that from this the pure <u>cis</u>-3,5-bis(triphenylphosphonium)cyclopentene dibromide LXXVIII could be prepared following the scheme shown below:
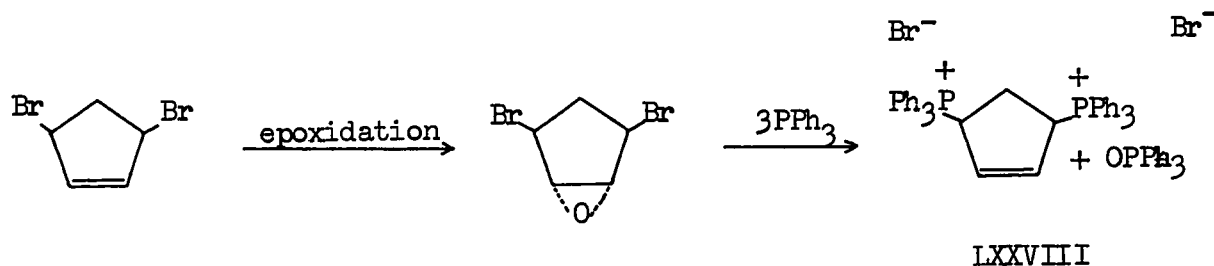


LXXVIII

If the salt LXXVIII could be isolated it could be compared with the salt or salts produced in the usual ylid synthesis and the conditions under which it would give the ylid could be studied. However, this project did not meet with much success as it was found that it was extremely difficult to obtain the epoxide in the pure form. It was always accompanied by varying amounts of the starting dibromide.

## Protonation Studies:

Another phase of the present investigation was the study of the protonation of the cyclopentadienylides. Protonation of a cyclopentadienylide XVII would produce the conjugate acid(s) of the ylid for which three tautomeric structures LXXIXa, LXXIXb and LXXIXc must be considered if protonation takes place in the five-membered ring. The methods which have been used in studying these protonations were to observe the nmr spectrum of the ylid directly in trifluoroacetic acid[81] or to observe the nmr spectrum of the protonated species such as the perchlorate of the ylid in trifluoroacetic acid[82].



XVII          LXXIXa          LXXIXb          LXXIXc
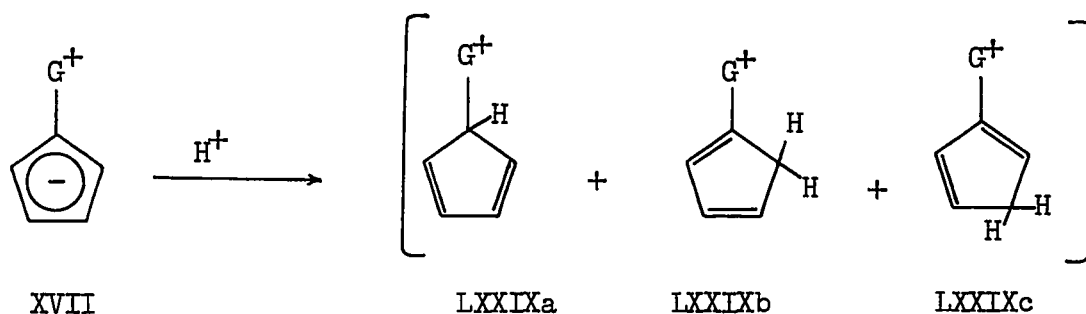
Protonation of 2-cyclopentadienylidene-1,2-dihydro-1-methyl-pyridine (XVIIe) was shown to give a mixture of the cations LXXXa and LXXXb in the ratio of 2:1, with little or no LXXXc[81]. The nmr spectrum of XVIIe in trifluoroacetic acid showed two signals assignable to the



XVIIe          LXXXa          LXXXb          LXXXc

              68%            32%            0%
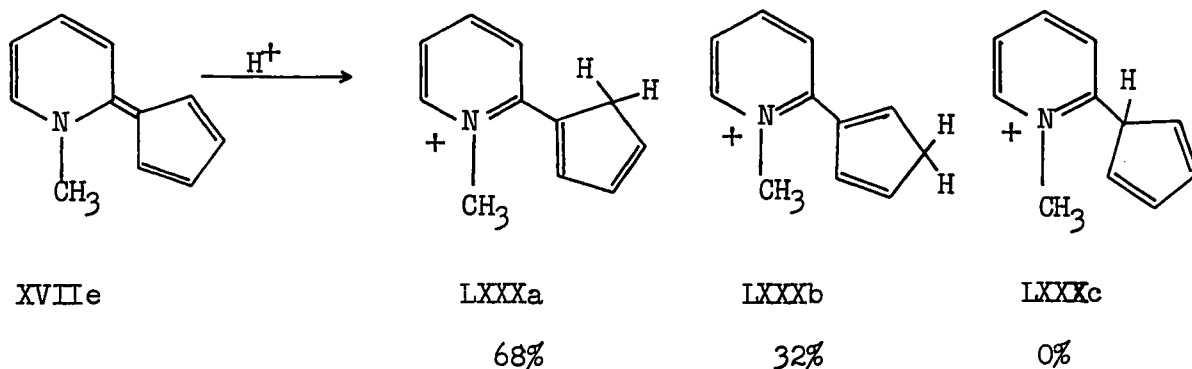
methylene protons of the five-membered ring. The signal at higher field

( $\delta$ 3.22) was assigned to the methylene protons in LXXXb and that at

lower field ( $\delta$ 3.52) was assigned to the methylene group in LXXXa.

These assignments were made on the grounds that the methylene group

LXXXa would be preferentially deshielded by the ring current in the

pyridinium ring. The preparation of the conjugate acids LXXXa and LXXXb

is in accord with the relative stabilities that might be expected on

qualitative grounds for the series of cations LXXXa > LXXXb > LXXXc,

since this is the order of decreasing extent of conjugation.

The nmr spectrum of 1-butyl-4-cyclopentadienylidene-1,4-dihydro-

2,6-dimethylpyridine perchlorate LXXXI in trifluoroacetic acid showed

the presence of two conjugate acids LXXXIa and LXXXIb[82]. In this case it



| LXXXIa | LXXXIb | LXXXIc |
|--------|--------|--------|
| 65% | 35% | 0% |
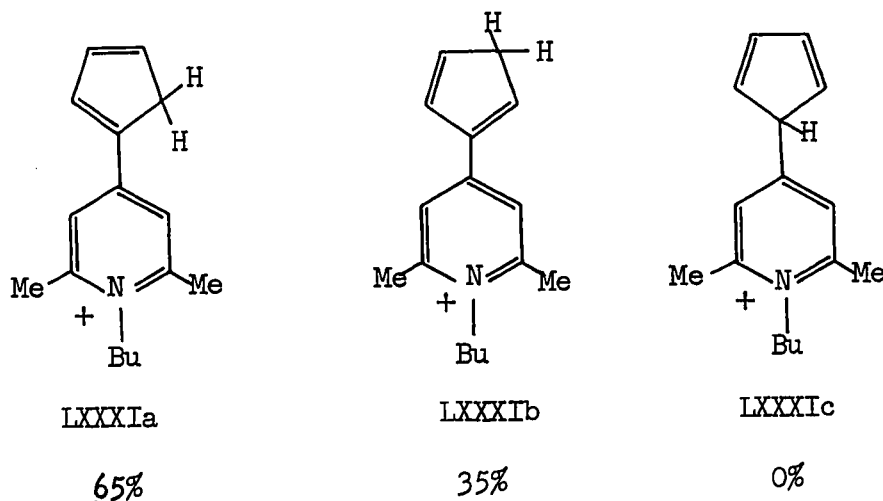
was observed that the methylene absorption of the minor component LXXXIb

appeared at a lower field ( $\delta$ 3.53) than that of its tautomer (LXXXIa)

which appeared at $\delta$ 2.9. Here also the criterion of stability (major product)

was assumed to be that based on the extent of conjugation.

In the present study protonations of triphenylphosphonium-

cyclopentadienylide (XVIIc), trimethylammoniumcyclopentadienylide (XVIIb)

pyridiniumcyclopentadienylide (XVIId) and the 1:1 adducts of

triphenylphosphoniumcyclopentadienylide with phenylisocyanate (XXX),

phenylisothiocyanate (XXXI) and acetylenedicarboxylate (XXXII) were

investigated. The nmr spectra of these products as well as those of

2-phenylazotriphenylphosphoniumcyclopentadienylide (XVIII) and

(cyclopentadienylhydrazono)-triphenylphosphorane (XVIIf) were recorded

in trifluoroacetic acid solvent. The nmr spectra indicate that only

in the cases of the unsubstituted ylids (XVIIb and c) and in the cases

of the isocyanate and the isothiocyanate derivatives (XXX and XXXI) did

protonation occur in the five-membered ring.

In all cases, except those of XVIIf and XVIIIa, the nmr spectra

of trifluoroacetic acid showed signals in the region of $\delta$ 4.0- $\delta$ 3.0,

which were assigned to protons of methylene groups mainly on the basis

of their chemical shifts and integrated areas. In the nmr spectrum of



XVIIc     XVIIb     XVIIf     XXX

XXXI     XXXII     XVIIIa
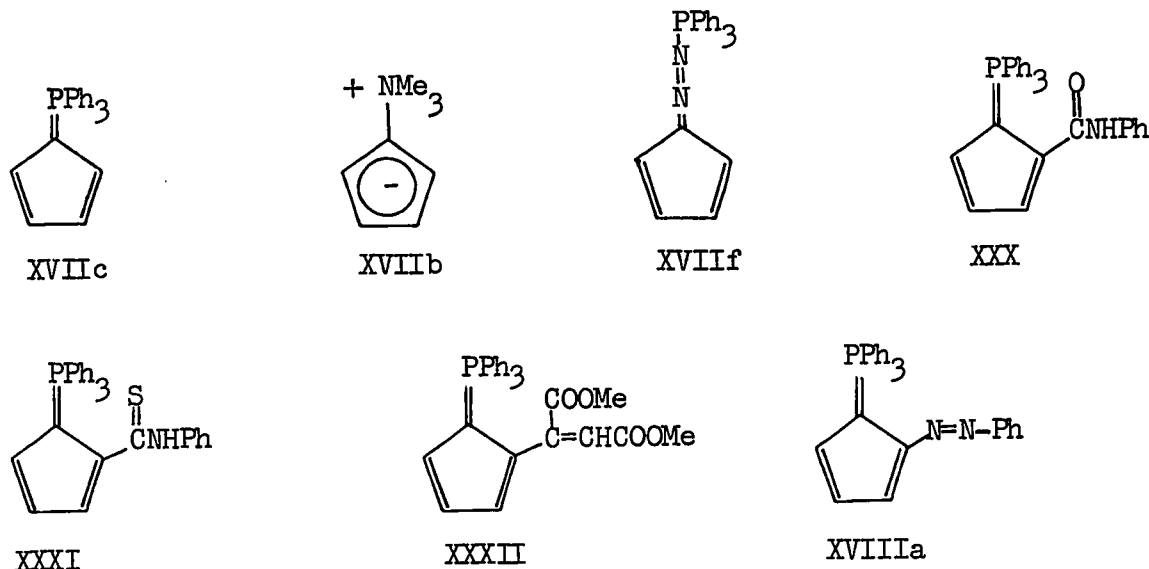
XVIIc in trifluoroacetic acid (nmr spectrum no. 2) the methylene protons

showed up as a slightly broad peak which upon examination at 50 Hz sweep

width was revealed as a composite of at least five overlapping peaks.

It was not possible to obtain any coupling constants from this multiplet. The signal appears as a multiplet because of the couplings to the other three protons in the five-membered ring as well as to phosphorus. On the basis of the integrated area of the peak (2 protons) one can rule out formula LXXXIIc as the structure of the protonated species. In view of the fact that other electrophilic reactions of the ylid, such as the diazo coupling and reactions with phenylisocyanate, phenylisothiocyanate, dimethyl-acetylenedicarboxylate, tetracyanoethylene and tricyanovinyl chloride, take place on the 2-position of the five-membered ring, the structure of the protonated species can be assigned the formula LXXXIIa. This is also the most conjugated of the three cations LXXXIIa, b and c.

In the nmr spectrum of the trimethylammoniumcyclopentadienylide
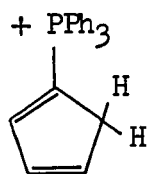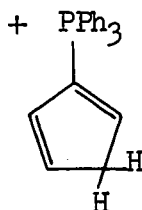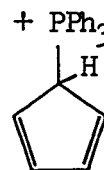


LXXXIIa                LXXXIIb                LXXXIIc
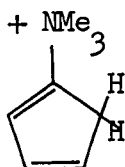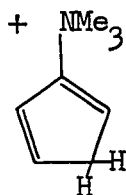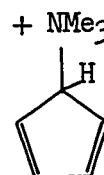


LXXXIIIa               LXXXIIIb               LXXXIIIc

in trifluoroacetic acid (nmr spectrum no. 12) the methyl protons appear as a sharp singlet at $\delta$ 3.6 and the vinylic protons in the five-membered ring as a complex multiplet between $\delta$ 6.4 and $\delta$ 7.0. The protons of the methylene group appear as a slightly broad peak at $\delta$ 3.3. Examination of the spectrum using 50 Hz sweep width at 100 MHz operating frequency revealed that this peak is a composite of four or five overlapping peaks.

The coupling constants of this multiplet could not be determined. The structure of the protonated species can be regarded as LXXXIIIa in analogy with the phosphorus ylid and for the same reasons.

In the case of pyridiniumcyclopentadienylide (XVIId) also the protonation occurs on the five-membered ring. This is revealed in the nmr spectrum of the compound in $CF_3COOH$ (nmr spectrum no. 13). There are two methylene signals in the spectrum at $\delta$ 2.65 and $\delta$ 2.40 in the proportion 53% and 47% respectively. The conjugate acids produced by
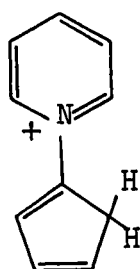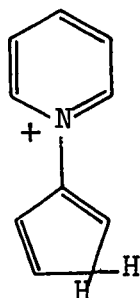
LXXXIVa                LXXXIVb

protonation here may reasonably be represented as LXXXIVa and LXXXIVb. However, it is difficult to assign structures to the two conjugate acids on the basis of the chemical shift of their methylene protons. It is interesting to note that the methylene protons here are considerably more shielded than in the other cases and that the two conjugate acids are produced to the same extent approximately.

Protonation of the 1:1 adduct of the XVIIc and dimethylacetylene-dicarboxylate takes place not in the five-membered ring but in the dicarbomethoxyvinyl substituent. This is evident from a comparison of the nmr spectra of the adduct (XXXII) in $CDCl_3$ (nmr spectrum no. 10) and in $CF_3COOH$ (nmr spectrum no. 11). The signal for the vinylic proton in the substituent at $\delta$ 4.7 in the spectrum in $CDCl_3$ vanished in the spectrum

of the product in $CF_3COOH$. In trifluoroacetic acid there appeared a

$$
\begin{array}{cc}
\overset{\text{PPh}_3}{\underset{}{\|}}\!\!\bigcirc\!\!\overset{\text{COOMe}}{\underset{}{|}}\,\text{C=CHCOOMe} & \overset{+\;\text{PPh}_3}{\underset{}{|}}\!\!\bigcirc\!\!\overset{\text{COOMe}}{\underset{}{|}}\,\text{C-CH}_2\text{COOMe}\\
\text{XXXII} & \text{LXXXV}
\end{array}
$$
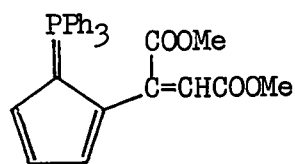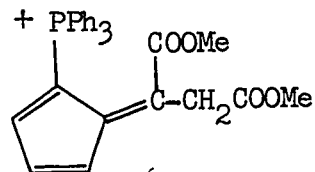
peak at $\delta\,3.75$ which corresponded to two protons. Also the integrated areas of the peaks in the aromatic region remained unchanged (18 protons); the signals for the protons in the five-membered ring shifted further downfield indicating the greater deshielding effect of the more positive phosphorus atom in the cation LXXXV, which is the protonated species here. Protonation in the corresponding tricyanovinyl derivative (XXVII) was also believed to take place in the vinyl substituent on the carbon atom furthest from the five-membered ring (cf. XXVIII)[57].

The nmr spectrum of the phosphinazine (XVIIf) was poorly resolved as the solution of the material in $CF_3COOH$ became viscous rapidly. The viscous solution was made mobile by adding $CDCl_3$ and the nmr spectrum of this solution indicated that no protonation took place in the five-membered ring. There was some indication of an N-H signal indicating protonation on one of the nitrogen atoms. However, no conclusive results could be obtained on this point as the material was not too stable in trifluoroacetic acid solutions.

In the case of the diazo derivative XVIIIa, the nmr spectrum in $CF_3COOH$ revealed that no protonation took place in the five-membered ring, but instead the protonation occurred on one of the nitrogen atoms as indicated by an N-H signal at $\delta\,8.4$ (nmr spectrum no. 4). This is in

agreement with the evidence (ir and chemical data) presented by Ramirez and Levy[42]. The hydrobromide of the diazo derivative was also prepared as described by these authors and its nmr spectrum in $CDCl_3$ (nmr spectrum no. 5) was very similar to that of the diazo derivative in $CF_3COOH$. It was observed that the N-H signal was a broad triplet with some fine structure in the case of the hydrobromide LXXXVI and that it was a broad
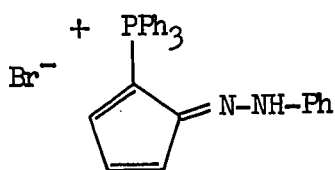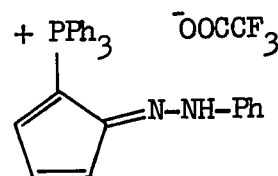


LXXXVI                    LXXXVII

singlet in the case of the trifluoroacetate LXXXVII in $CF_3COOH$, although the cation (the protonated species) is the same in both cases.

The isocyanate derivative XXX in $CF_3COOH$ revealed in its nmr spectrum (nmr spectrum no. 7) a single broad signal for the methylene protons at $\delta$ 3.9 (as in the case of the other ylids indicating that protonation did take place in the five-membered ring). As in the other cases the broadening of this signal is attributed to coupling with other protons in the five-membered ring as well as to the phosphorus atom. The isothiocyanate derivative XXXI in $CF_3COOH$ revealed in its nmr spectrum two separate broad methylene absorptions at $\delta$ 3.8 and $\delta$ 3.6 in approximately 3:2 ratio (cf. nmr spectrum no. 9), indicating that at least two protonated species are present in this case. In each case for protonation in the five-membered ring one can have the following possibilities:
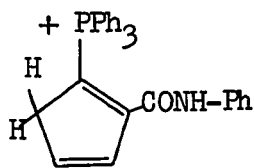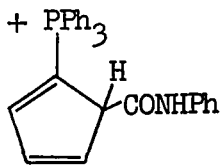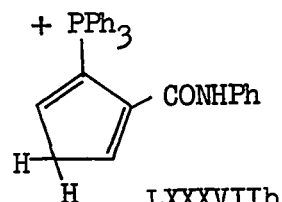
LXXXVIIa   LXXXVIId   LXXXVIIb
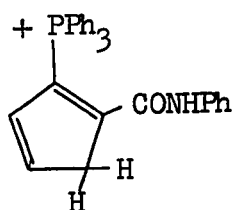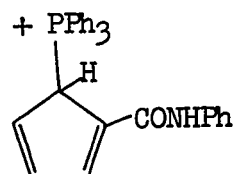
LXXXVIIc   LXXXVIIe
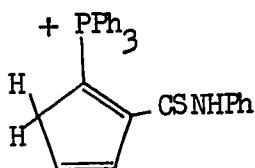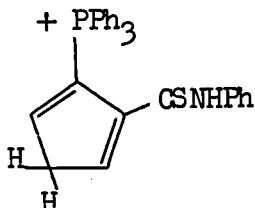
LXXXVIIIa   LXXXVIIIb   LXXXVIIIc
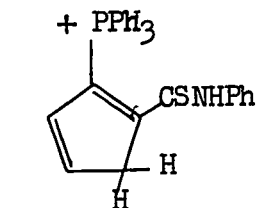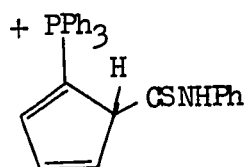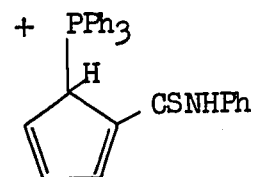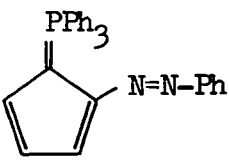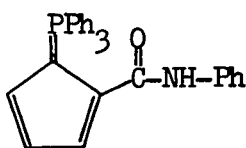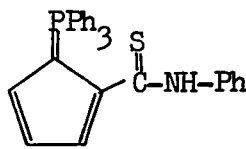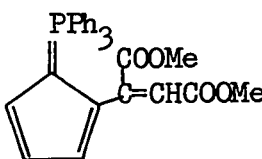
LXXXVIIId   LXXXVIIe

## Spectral Data on Protonations:

In considering the protonations of the compounds described above it is instructive to consider the uv spectra of these compounds in acidic solutions (ethanol solutions made acidic with $HClO_4$). The uv (cf. uv spectra nos. 1-3) and appropriate nmr data are summarized in Table IV.

Table IV. Spectral Data for Protonated Ylid Derivatives

| Ylid Derivative | Uv (EtOH; $HClO_4$) $\lambda_{max}$, nm | Nmr ($CF_3COOH$) $\delta$-values for methylene protons |
|---|---|---|
| PPh₃ N=N–Ph | 226 267 275 | ≠ |
| PPh₃ O ‖ C–NH–Ph | 335 | 3.9 |
| PPh₃ S ‖ C–NH–Ph | 335 410 | 3.8 3.6 |
| PPh₃ COOMe C=CHCOOMe | 295 | 3.7 |

≠ Protonation takes place on nitrogen (cf. ref. 42)

In protonated triphenylphosphoniumcyclopentadienylide the methylene group in the five-membered ring adjacent to the phosphorus atom appeared at $\delta$ 3.6. If this is taken as the standard chemical shift of a methylene group adjacent to a triphenylphosphonium group, then in the case of the isocyanate derivative the methylene protons are more

deshielded ( $\delta$ 3.8); for this reason one might consider structure LXXXVIIb or LXXXVIIc. It is observed that protonation shifts the $\lambda_{max}$ to longer wavelength compared to the unprotonated ylid derivative XXXI. This is suggestive of more extended conjugation in the protonated species as is the case in cation LXXXVIIc. Structures LXXXVIId and e (containing one tertiary hydrogen atom in each case) are ruled out on the basis of the chemical shifts and integrated areas for the peaks and also due to lack of the expected couplings for such structures. The uv spectrum of the isothiocyanate derivative XXXI also shows bathochromic shift upon protonation, indicating more extended conjugation in the protonated species. The predominant (more stable) species, showing methylene absorption at $\delta$ 3.8, is assigned the structure LXXXVIIIc on the basis of the same arguments as were advanced in the case of the isocyanate derivative. The minor (less stable) species is assigned the structure LXXXVIIIa as this is the more stable (more conjugated cation) one compared to LXXXVIIIb. Structures LXXXVIIId and LXXXVIIIe are ruled out for the same reasons as in the case of the isocyanate derivative. If these assignments are correct, then it is not well understood why the isocyanate derivative does not produce a species LXXXVIIIa. For unambiguous assignments of the structures further work involving phosphorus and proton-decoupling studies as well as variable temperature studies, is indicated.

Conclusion:

From the results available so far, it would seem that the electrophilic attack in the five-membered ring of the unsubstituted cyclopentadienylides takes place predominantly in the 2-position. In the case of sodium nitrocyclopentadienylide it was demonstrated that, as between 2- and 3-positions, kinetically controlled protonation of
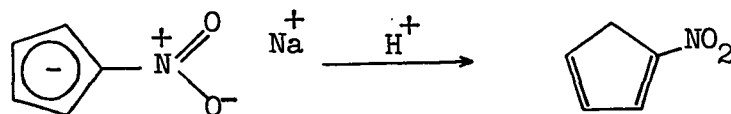
the anion occurs at the 2-position[83]. 1-Nitrocyclopentadiene is the sole product here. When there are two different substituents in the five-membered ring, all five positions in this ring are non-equivalent. In the case of the isocyanate derivative XXX and the isothiocyanate derivative XXXI, it would seem that protonation occurs preferentially in one position (adjacent to the amide substituent) in the former case and in two positions (adjacent to a substituent in each case) in the latter.

# SUMMARY

In connection with an investigation of some aspects of the nonbenzenoid aromaticity of the five-membered ring system in cyclopentadienylides, the following ylids were prepared by known methods.



$$\overset{+}{G} = \overset{+}{PPh_3}, \quad \overset{+}{NMe_3}, \quad -\overset{+}{N=N-PPh_3},$$

(R = H, 2-Me, 3-Me, 4-Me)
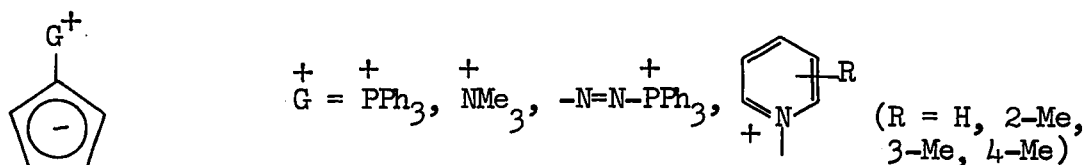
Three new reactions of triphenylphosphoniumcyclopentadienylide involving phenylisocyanate, phenylisothiocyanate and dimethylacetylene-dicarboxylate have been discovered. The structures of these new compounds have been established, from a consideration of their spectral properties and analytical data, to be the following.
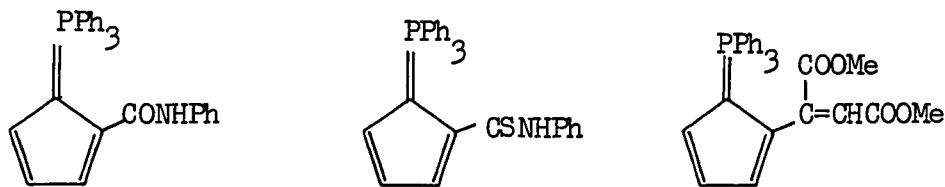


The isocyanate adduct has been shown to undergo protonation in the five-membered ring in trifluoroacetic acid to give a single protonated species. From the evidence available the site of protonation is believed to be the position adjacent to the amide substituent. The isothiocyanate adduct showed the presence of two protonated species in

trifluoroacetic acid and the sites of protonation here are suggested to be those adjacent to the two substituents in the five-membered ring. In contrast to these derivatives the acetylenedicarboxylate adduct protonates on the side chain as shown by the nmr spectrum of the product in trifluoroacetic acid. It has also been demonstrated that in triphenylphosphonium and in trimethylammonium cyclopentadienylides the protonation takes place preferentially in the 2-position to give a single species in each case.

Attempts at effecting dipolar addition reactions of nitrile oxides with the ylids failed. Although there was some evidence of a Wittig-type reaction with (cyclopentadienylhydrazono)triphenylphosphorane, several attempts at generating new "stable" nonbenzenoid aromatic systems from this ylid using tropone, diphenylcyclopropenone and p-dimethylamino-benzaldehyde were unsuccessful.

In an attempt to gain some insight into the mechanism of formation of the ylids, the "di-salts" which are the precursors of trimethylammonium, pyridinium and 2-picolinium cyclopentadienylides have been isolated and their nmr spectra examined. Although the structures of the salts have not been established unambiguously, it seems that they all have the same "trans-1,2-bis-3-cyclopentene" structure, in accordance with the already established mechanism of an $S_N2$ reaction followed by an $S_N2'$ reaction on the 3,5-dibromocyclopentenes. A mechanism for the formation of the ylid from the di-salt is also postulated.

# EXPERIMENTAL

Reagents and Chemicals:- The reagents and chemicals used in the present study were obtained from various commerical sources and indicated below:

Aldrich Chemical Co., Inc., Milwaukee, Wisconsin:- Cyclohexylisocyanate, Chloroacetonitrile.

Allied Chemicals Canada Ltd:- Perchloric acid.

Anachemia Chemicals Ltd., Montreal, Quebec:- Dioxane.

British Drug Houses (Canada) Ltd:- Bromine, Hydroxylamine hydrochloride.

Canadian Laboratory Supplies Ltd., (Matheson, Coleman and Bell):-
Methyl iodide, Selenium dioxide, p-toluenesulfonyl chloride, sodium azide.

Fisher Scientific Co., Ltd. (Eastman):- dimethylacetylene dicarboxylate, p-dimethylaminobenzaldehyde,2-, 3-, and 4-picolines, phenylisocyanate, phenylisothiocyanate, pyridine.

J.T. Baker Chemical Co., Phillipsburg, New Jersey:- carbon disulfide, 1,3,5-cycloheptatriene, dicyclopentadiene, dimethylamine, triethylamine.

K and K Laboratories, Plainview, N.Y.:- 1,3-diphenyl-2-propanone.

Mallinkrodt Chemical Works, Pointe Claire, Quebec:- potassium phosphate monobasic.

M and T Chemicals, Inc., Rahway, New Jersey:-triphenyl phosphine.

Most reagents were freshly distilled or recrystallized before use.

Melting Points and Boiling Points:- All melting points and boiling points reported are uncorrected. Melting points were taken on a Gallenkamp MF-370 instrument.

Elemental Analyses:- Elemental microanalyses were performed

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by Schwarzkopf Microanalytical Laboratory, Woodside, New York and by

Dr. R.T. Rye of this Department using an F and M Model 185 CHN Analyser.

Ir and Uv Spectra:- All ir spectra were obtained using a

Perkin-Elmer Model 137 spectrometer and a Beckman IR-8 double-beam

recording spectrometer with sodium chloride optics. Frequencies reported

are accurate to $\pm$ 10 cm$^{-1}$. Uv spectra were recorded on a Beckman DB

instrument using 95% ethanol or water as solvents. Acidification of

the solutions were done by using 70% perchloric acid in acetic acid.

Wavelengths reported are accurate to $\pm$ 5 nm.

Nmr Spectra:- All nmr spectra were recorded using Varian A-60A

or HA-100 spectrometers on undegassed samples (as solutions in CDCl$_3$,

CF$_3$COOH, or D$_2$O). All chemical shifts are expressed in ppm ( $\delta$ )

relative to tetramethylsilane used as an internal standard. Spin-spin

coupling constants were measured from spectra recorded at 50 Hz sweep

widths.

Triphenylphosphoniumcyclopentadienylide[39].— To a solution of

22 g (0.33 mol) of freshly cracked cyclopentadiene in 30 ml of chloroform

bromine (54 g; 17.5 ml) in 30 ml of chloroform was added dropwise with

stirring. Bromination was carried out in an ice-salt bath (-6 to -10°).

The solution was then diluted with 50 ml of chloroform and treated with

174.6 g of triphenylphosphine in 250 ml of chloroform at 0°. The reaction

mixture was gently refluxed for 6 hr and then allowed to remain at room

temperature for 12 hr. The solvent was removed under reduced pressure to

give a glassy red solid. This red solid was dissolved in 300 ml of

methanol with heating. To the mixture, cooled in an ice-bath, a solution

of sodium hydroxide (50 g in 200 ml of water) was added. A brown oil

formed which was decanted from the supernatant yellow layer, treated with

400 ml of methanol and refrigerated to allow crystallization of a yellow
precipitate. The product was recrystallized from 150 ml of chloroform
and 500 ml of methanol. After filtration, the product was washed with
methanol and dried in air giving 26.3 g; (24.4%) of the ylid as a light
yellow solid, mp 229-231°; the infrared spectrum (KBr) was identical to
that reported.

### Reaction of Triphenylphosphoniumcyclopentadienylide with

Phenylisothiocyanate.- To the clear yellow solution of 7.2 g (0.04 mole)
of purified triphenylphosphoniumcyclopentadienylide dissolved in 250 ml of
dry benzene were added 5.5 g (0.04 mole) of freshly distilled phenylisothio-
cyanate in 40 ml of dry benzene. The mixture was refluxed for 5 hr and became
dark brown. On cooling to room temperature a yellow solid crystallized
which was filtered and washed with methanol giving 5.5 g of crude
product. Reduction of the filtrate to one-half the volume yielded an
additional 2.04 g of the product. From 2.12 g of the product
chromatographed on an alumina column (Fisher, 80-200 Mesh, Adsorption)
with chloroform as eluent 1.5 g of yellow crystalline solid was recovered.
Recrystallization of the remaining crude product from chloroform-methanol
gave an additional 2.68 g of the same product. The combined yield of the
pale yellow crystalline solid mp 218-219° (decomp) was 4.18 g (33%). Ir
(CHCl$_3$) 3400 cm$^{-1}$ (N-H), 1500 cm$^{-1}$ (N-H), 1435 cm$^{-1}$ (P-Ph), 1270 cm$^{-1}$ (C=S);
uv (95% ethanol) $\lambda_{max}$ 380 nm ($\epsilon$ 26,280); (CDCl$_3$): one-proton multiplets
at δ 5.9 and δ 6.3, 21-proton complex multiplet centered around δ 7.4, one-
proton singlet at δ 8.7 (N-H).

Anal. Calcd. for C$_{24}$H$_{20}$PNS: C,78.05; H,5.24; N,3.04.

Found: C,77.67; H,5.35; N,3.43.

An identical product (7.84 g: 61.7%) was obtained when the procedure was

repeated using twice the molar amount of phenylisothiocyanate.

## Reaction of Triphenylphosphoniumcyclopentadienylide with

Phenylisocyanate:- In a 500 ml flask equipped with a Dean-Stark condenser, 6.60 g (.02 mole) of purified triphenylphosphoniumcyclopentadienylide was added to 250 ml of benzene. Phenylisocyanate (2.38 g; 0.02 mole) was then added to the yellow solution and the mixture was refluxed 3.5 hr. A color change to dark red occurred and a red-orange solid (5.85 g) slowly separated from the solution. After 12 hr the product was filtered; evaporation of the filtrate to 20 ml gave an additional 1.1 g of the product. The combined crude product (6.95 g) was recrystallized from 75 ml of benzene to give 5 g of a light yellow solid. Further recrystallization from 60 ml of benzene gave 3.6 g of a very light yellow solid. A final recrystallization from 120 ml chloroform-methanol (1:5,v/v) gave a white solid 2.2 g (24.5%) mp 236-237°; ir (chloroform) 1630 $cm^{-1}$ (carbonyl stretching), 1510 $cm^{-1}$ (amide N-H), 1435 $cm^{-1}$ (P-Ph), uv (95% ethanol) $\lambda_{max}$ 335 nm ($\epsilon$ 30,815); nmr (CDCl$_3$) (ppm) one-proton multiplets at $\delta$ 5.88 and $\delta$ 6.3, 22 proton-complex at $\delta$ 6.8-7.8. Upon storage the material acquired a light pink color. (Retention of chloroform prevented a satisfactory elemental analysis). Upon repetition of the above experiment with twice the amount of phenylisocyanate an identical product was obtained.

## Attempted Reaction of Triphenylphosphoniumcyclopentadienylide

with Cyclohexylisocyanate:- To a solution of the ylid (3.3 g) in dry benzene (150 ml) was added 1.7 g of cyclohexylisocyanate in 30 ml benzene and the mixture refluxed for 6 hr. On evaporating the reaction mixture to dryness a solid (3.2 g) was recovered and identified as unreacted triphenylphosphoniumcyclopentadienylide by ir spectrum and mp.

The method of Depoorter, Nys and VanDormael[2] with a few modifications

as described was also used. To a mixture of 1.65 g (.005 mole) of the

ylid and equimolar cyclohexylisocyanate (0.63 g) in 30 ml of benzene

were added 25 ml of acetic anhydride and 1.4 ml of triethylamine

(1.01 mole). After refluxing for 30 min the solution changed from

yellow to dark brown. Upon reducing the volume of the reaction

mixture the unreacted ylid (0.8 g) precipitated and was removed

by filtration. Evaporation of the filtrate yielded a tarry residue

from which no identifiable product could be isolated.

Reaction of Triphenylphosphoniumcyclopentadienylide with

Dimethylacetylenedicarboxylate.- A solution of dimethylacetylene

dicarboxylate (4.7 g) in chloroform (5 ml) was added dropwise to a

cooled solution (ice bath) of 10 g of triphenylphosphoniumcyclopenta-

dienylide in 100 ml of chloroform. The operation was carried out

under an atmosphere of nitrogen. A color change from orange to red

occurred. Evaporation of the mixture to dryness gave a glassy red

residue which when heated dissolved in 125 ml of ethanol. Upon

refrigeration this solution yielded 3.7 g of a yellow crystalline

solid. Evaporation of the filtrate to dryness gave a red resinous

material from which additional crystalline product (0.72 g) was

obtained on extraction with hot ethanol. Recrystallization of the

combined crude product from ethanol gave 1.9 g (13.3%) of a yellow

crystalline solid mp 232-234°; ir (CHCl$_3$) 3330 cm$^{-1}$, 1730 cm$^{-1}$ and

1695 cm$^{-1}$ (C=O), 1430 cm$^{-1}$ (P-Ph); uv (95% ethanol): $\lambda_{max}$ 390 nm

($\epsilon$ 74,160); nmr (CDCl$_3$), 3-proton singlets at $\delta$ 3.3 and $\delta$ 3.9

(O-CH$_3$), 1-proton singlet at $\delta$ 4.7 (vinylic), 1-proton multiplets at

$\delta$ 6.0, $\delta$ 6.4 and $\delta$ 6.8 and a complex 15-proton multiplet

centered around $\delta$ 7.5.

<u>Anal</u>. Calcd. for $C_{29}H_{25}O_4P$:  C,74.40; H,5.04; P,6.62

Found:  C,74.71; H,5.45; P,6.62.

Treatment of this product with a second equimolar amount of

dimethylacetylenedicarboxylate did not result in further addition;

unreacted starting material was recovered.

<u>Attempted Reaction of Triphenylphosphoniumcyclopentadienylide</u>

<u>with 1-Phenyl 3-Propynone</u>.-  1-Phenyl-3-propynone (1.0 g) in 25 ml of

chloroform was added dropwise to a cooled ($0^o$) and stirred solution

of the ylid (2.0 g) in chloroform.  After refrigeration for 12 hr

the reaction mixture was allowed to stand at room temperature for a

further 24 hr.  Upon concentration of the reaction mixture only the

unreacted ylid was recovered.  This was redissolved in 35 ml of

chloroform and refluxed with 1.0 g of the acetylenic ketone for

2 hr.  Removal of the solvent at reduced pressure gave a dark residue

from which 1.5 g of the starting ylid was isolated.

<u>Attempted Reaction of Triphenylphosphoniumcyclopentadienylide</u>

<u>with Chloroacetonitrile</u>.-  A mixture of 3.11 g (9.5 mmole) of the ylid

in 25 ml of chloroform and 2.79 g (37 mmole) of chloroacetonitrile was

refluxed under nitrogen for 6 hr.  The color of the solution changed

from yellow to red.  On evaporation of the reaction mixture to

dryness 2.9 g of a red amorphous solid was recovered which was

identified (ir) as the starting ylid.

<u>Triphenylphosphonium-(2-phenylazo)-cyclopentadienylide</u>[84].-

A benzenediazonium chloride solution was prepared from 5.6 g of aniline,

15.2 ml of concd. hydrochloric acid, 68 g of ice and 4.2 g of sodium

nitrite in 100 ml of water.  Addition of ca. 28 g of sodium acetate

raised the pH to 5-6 and produced a yellow precipitate. To this mixture was added, with stirring, a solution of triphenylphosphonium-cyclopentadienylide (19.6 g) in methylene chloride (500 ml); the temperature was kept at 0-5° during the rapid addition. The methylene chloride phase became red immediately. After 30 minutes at 0°, the mixture was treated with 5% aqueous sodium hydroxide (60 ml), the methylene chloride layer was separated and the aqueous layer was extracted with methylene chloride. The combined methylene chloride solutions were dried over sodium sulfate, filtered, and evaporated to dryness in vacuo. The residue on treatment with 800 ml of methanol yielded insoluble orange crystals. This product was recrystallized from benzene-methanol to give a red crystalline solid (11.8 g; 45.8%), mp 238-240°. The infrared spectrum of the product was identical to that reported.

Attempted Reaction of Triphenylphosphonium-(2-phenylazo)-cyclopentadienylide with Phenylisocyanate.- To a solution of 1.28 g of the triphenylphosphonium-(2-phenylazo)-cyclopentadienylide in 100 ml of dry benzene 0.7 g of phenylisocyanate was added and the resulting red mixture was refluxed for 5 hr. The residue obtained on evaporation of the solution to dryness was washed with ether and was identified as unreacted triphenylphosphonium-(2-phenylazo)-cyclo-pentadienylide (1.2 g).

Diphenylcyclopropenone[85].- To a solution of 35 g (0.165 mole) of dibenzyl ketone in 125 ml of glacial acetic acid was added with stirring over 15 min., a solution of 55 g of bromine (0.33 mole) in 250 ml acetic acid. After the addition was complete, the mixture was stirred for an additional 5 min and then poured into 0.5 l of water.

Solid sodium sulfite was added in small portions until the initial
yellow color of the solution was discharged, and the mixture was
allowed to stand for 1 hr. The mixture of isomers (54 g) of
meso - and dl - α,α' dibromodibenzyl ketone, was dissolved in 250 ml
of methylene chloride without recrystallization. This solution was
added with stirring over 1 hr to 50 ml triethylamine at room
temperature. The red mixture was stirred for an additional 30 min,
extracted with two 150 ml portions of 3 N hydrochloric acid
(discarded), and the organic phase was transferred to a flask and
cooled in an ice bath. A cool solution of 50 ml of sulfuric acid
in 25 ml of water was slowly added. The pink precipitate of diphenyl-
cyclopropenone bisulfate was partially tar-like. This product was
filtered then returned to the flask along with 125 ml of methylene
chloride and 250 ml of water, and 2.5 g of solid sodium carbonate was
added in small portions. The aqueous layer was extracted with two
150 ml portions of methylene chloride. The combined organic layers
were dried over magnesium sulfate and evaporated to dryness. The
impure pink diphenylcyclopropenone was recrystallized by repeated
extractions with boiling cyclohexane, the solution being decanted
from a reddish oily impurity. On cooling the solution deposited
white crystals (3.05 g) of diphenycyclopropenone, mp 118-119°.

Preparation of Tropone[86].- To a solution of potassium
dihydrogenphosphate (6.75 g, 0.05 mole) in water (16 ml) was added
1,4-dioxane (165 ml), 1,3,5-cycloheptatriene (21.5 g, 0.23 mole),
and selenium dioxide (26.5 g, 0.24 mole). The mixture was heated
on an oil bath, at 90° for 15 hr, allowed to cool to room
temperature, and then filtered. The brown filtrate was poured

into water (380 ml) and extracted three times with 125 ml portions of methylene chloride. The organic extract was washed with 10% sodium bicarbonate, dried over magnesium sulfate, filtered, and concentrated in vacuo to a dark brown liquid. Distillation of this liquid gave 6.53 g (25.5%) of pale yellow tropone bp 74°/1.5 mm. The infrared spectrum was as reported by Doering and Detert[87].

Attempted Reaction of Tropone with Triphenylphosphonium-cyclopentadienylide.- A mixture of 1.0 g of the ylid and 0.35 g of tropone in 20 ml of dichloromethane was refluxed for 3 hr during which the solution became red-brown. The red residue obtained on evaporation of the solvent to dryness was washed with methanol and resulted in the recovery of 0.44 g of the unreacted ylid. The removal of solvent in vacuo from the filtrate yielded a dark resinous material (0.8 g), from which no pure product could be isolated.

Attempted Reaction between Triphenylphosphoniumcyclo-pentadienylide and Diphenylcyclopropenone.- To 0.93 g of the ylid dissolved in 75 ml of benzene was added 0.5 g of diphenylcyclo-propenone in 30 ml of benzene and the mixture was refluxed under nitrogen for 4 hr. Evaporation of the solution gave a tarry residue from which 0.5 g of a solid was isolated and was identified as the starting ylid. The filtrate on evaporation yielded a dark brown residue from which no identifiable product could be isolated.

Pyridiniumcyclopentadienylide.- To a solution of dibromo-dioxane (6.2 g) in 32 ml of anhydrous pyridine cooled to 0° freshly distilled cyclopentadiene (4 ml) was added. After shaking for ca. three min. the reaction mixture deposited a precipitate of cyclopentene-bis-pyridinium bromide. The stable brown solid,

7.14 g (41.6%) was filtered and washed with anhydrous ether and stored in a desiccator over calcium chloride. Treatment of an aqueous solution of the bis-pyridinium salt with concd. sodium hydroxide gave a precipitate of lustrous copper-red crystals (90% yield) of the ylid which could be extracted into chloroform and used for further experiments.

α,β- and γ-Picolinium Cyclopentadienylides. Method A.-
These ylids were similarly obtained by the action of 1-,2-, and 3-picolines on 3,5-dibromocyclopentene and were extracted into chloroform immediately after their liberation from the corresponding salts with base.

α- and β-Bis-picolinium salts. Method B.- The corresponding cyclopentene-bis-picolinium bromides of 2-, and 3-, picolines were isolated in yields of 13.3% and 22.4% respectively. Cyclopentene-bis-4-picolinium bromide could not be isolated as a solid but only as an oil. From the stable salts the corresponding ylids could be precipitated by addition of concd. sodium hydroxide solution.

Pyridiniumcyclopentadienylide. Method A[40].- Freshly distilled cyclopentadiene (8.65 g, 0.131 mole) dissolved in 33 ml of chloroform was cooled in ice-salt, and bromine (20.3 g, 6.5 ml) in chloroform (30 ml) was added during 1 hr, with stirring. The solution of dibromocyclopentene was added to a solution of 23.4 ml of pyridine (22.4 g, 0.28 mole) in chloroform (20 ml) and set aside for 12 hr. Chloroform was then distilled off at room temperature, the dark brown oil was extracted with water (ca. 80 ml) and the extract was made alkaline by the addition of 10% sodium hydroxide

(50 ml). Immediately a lustrous red-brown precipitate of pyridinium-cyclopentadienylide was formed (18.65 g, 58.5%). The ylid was stored under nitrogen in a desiccator.

Pyridiniumcyclopentadienylide. Method B.- The procedure of Baranetskaya, Kursanov and Setkina[88] which allows isolation of the stable intermediate bis-pyridinium salt was used.

Dioxan Dibromide[89].- Bromine (40 g) was added with vigorous stirring to dioxan (20 g) cooled in an ice bath. The solidified mixture was then transferred into light petroleum (300 ml, bp 40°), precooled to -20°. The yellow precipitate was rapidly filtered off under suction and freed from solvent under vacuum and stored at 0° due to its volatility. This yellow solid (50 g), mp 65-67°, was used without further purification.

Diazocyclopentadiene[90].- A mixture of 20 g of p-toluenesulfonyl azide, 8 ml of freshly distilled cyclopentadiene and 9 ml of diethylamine was left at 0° for 3 days. After adding 50 ml of water the dark mixture was extracted several times with pentane. The combined extracts were washed until neutral and then dried over anhydrous sodium sulfate. Diazocyclopentadiene was not isolated in pure form because of its explosiveness but the concentrated pentane extracts were used directly for further reactions.

(Cyclopentadienylhydrazono)triphenylphosphonane.- Triphenylphosphine (25 g) in 100 ml of ether was added to a solution of diazocyclopentadiene in pentane prepared from 20 g of p-toluenesulfonyl azide, and after 1 hr orange crystals separated. Filtration and drying yielded 25.4 g (73%) of product mp 148°. The infrared spectrum of the product was identical to the one reported.

Attempted Reaction of Diazocyclopentadiene with Tropone.-
The solvent was evaporated in vacuo from a pentane solution (17 ml)
of diazocyclopentadiene. To the orange liquid (ca. 0.75 g) thus
obtained was added tropone (0.86 g) in dichloromethane (5 ml) and
the mixture was refluxed for 5.5 hr. Comparison of the ir spectra
of the mixture previous to and after refluxing showed that no
change had taken place.

Attempted Reaction of Diazocyclopentadiene with Diphenyl-
cyclopropenone.- A pentane solution (8 ml) of diazocyclopentadiene
was refluxed with 0.5 g of diphenylcyclopropenone in 5 ml
dichloromethane for 5 hr with no color change. The ir spectrum of the
residue obtained after evaporation of the solvent showed that no
reaction had taken place.

Attempted Reaction of Diazocyclopentadiene with 1-Phenyl-
3-Propynone.- The solvent was removed from a pentane solution of
diazocyclopentadiene (ca. 1.7 g of diazocyclopentadiene), and then
added to a solution of 2.2 g of the acetylenic ketone in dichloro-
methane (6 ml). The mixture was refluxed for 1 hr. The infrared spectrum
of the mixture indicated that no reaction had occurred.

Attempted Reaction of (Cyclopentadienylhydrazono)triphenyl-
phosphorane with Phenylisocyanate.- To a solution of the ylid (3.5 g)
dissolved in dry benzene (100 ml), phenylisocyanate (1.35 g) in 40 ml
of benzene was added dropwise at 0°, with stirring. The operation
was carried out under an atmosphere of nitrogen. The solvent from the
red-brown reaction mixture was removed in vacuo and the dark brown
residue was refluxed with benzene. On evaporation to dryness the
benzene extract yielded a very small amount of crystalline product

whose mp and ir spectra were identical to those of triphenyphosphine oxide. No identifiable product could be isolated from the dark benzene-insoluble residue.

Attempted Reaction of (Cyclopentadienylhydrazono)triphenyl-phosphorane with phenylisothiocyanate.- A mixture of 3.5 g of the ylid and 1.35 g of phenylisothiocyanate was refluxed for 1 hr. The brown reaction mixture was evaporated to dryness to give a dark resinous product. A benzene extract of this material yielded very small quantities of a crystalline product which was identified (mp and ir spectrum) as triphenylphosphine sulfide.

Attempted Reaction of (Cyclopentadienylhydrazono)triphenyl-phosphorane with cyclohexylisocyanate.- A black tarry residue was obtained upon refluxing the ylid (2 g) with cyclohexylisocyanate (1 g) for 6 hr and then removing the solvent. As in the case of phenylisocyanate reaction small quantities of triphenylphosphine oxide were isolated and identified (ir spectrum) from a benzene extract of the tarry residue.

The Reaction of (Cyclopentadienylhydrazono)triphenyl-phosphorane with Dimethylacetylene dicarboxylate.- To a solution of the ylid (2.0 g) in chloroform (35 ml) was added a solution of dimethylacetylene dicarboxylate (0.9 g) in chloroform at $0^{o}$, with stirring. The operation was carried out under an atmosphere of nitrogen. The reaction mixture was kept at $0^{o}$ for 12 hr and then evaporated to dryness at reduced pressure yielding a tarry residue from which no pure product could be isolated.

Attempted Reaction of (Cyclopentadienylhydrazono)triphenyl-phosphorane with 1-Phenyl-3-propynone.- A mixture of the ylid

(2.2 g) and the acetylenic ketone (1 g) in chloroform (100 ml) was refluxed during 3 hr. The solvent from the brown reaction mixture was then removed and the residue washed with ether. The solid that was recovered (1.8 g) was identified as the unreacted ylid (ir spectrum).

Attempted Reaction of (Cyclopentadienylhydrazono)triphenyl-phosphorane with Tropone.- The ylid (1.8 g) was refluxed with tropone (0.53 g) in dry benzene (85 ml) during 3 hr. The residue (1.5 g) obtained on evaporation of the solvent was washed with ethanol and was identified as the unreacted ylid (ir spectrum).

Attempted Reaction of (Cyclopentadienylhydrazono)triphenyl-phosphorane with diphenylcyclopropenone.- A mixture of 1.1 g of the ylid and 0.5 g of diphenylcyclopropenone in 100 ml of benzene was refluxed for 17 hr. The brown residue obtained on the removal of solvent was washed with benzene to yield 0.7 g of a solid which was identified as the starting ylid (ir spectrum).

Attempted Reaction of (Cyclopentadienylhydrazono)triphenyl-phosphorane with Benzonitrile oxide.- A solution of benzhydroximic chloride (0.8 g) in chloroform (14 ml) was added dropwise with stirring, at $0^{o}$, to a solution of the ylid (1.7 g) and triethylamine (0.5 g) in chloroform (25 ml). Stirring was continued during 2 hr at $0^{o}$ with a color change to dark red and the mixture refrigerated for 24 hr. Evaporation of solvent under reduced pressure yielded a resinous product which was chromatographed on a alumina column with chloroform eluent. The major fractions gave tars; the final fraction an ir sample of triphenylphosphine oxide.

Attempted Reaction of (Cyclopentadienylhydrazono)triphenyl-phosphorane with Carbon Disulfide.- A solution of the ylid (2 g) and

carbon disulfide (30 ml) in chloroform (25 ml) was maintained under

nitrogen at room temperature for 3 days. From the black amorphous

precipitate which formed then was filtered no pure product could be

isolated. Evaporation of the filtrate yielded sufficient triphenyl-

phosphine sulfide to be detected by an infrared spectrum.

Attempted Reaction of (Cyclopentadienylhydrazono)triphenyl-

phosphorane with p-Dimethylaminobenzaldehyde.- A solution of the ylid

(3.5 g) and freshly recrystallized p-dimethylaminobenzaldehyde (1.5 g)

in benzene was refluxed for 9 hr. Removal of solvent yielded

unreacted ylid (3.3 g). The method of Depoorter, Nys and VanDormael[92]

with a few modifications was also attempted. To a mixture of the ylid

(1.75; 5 mmole) p-dimethylaminobenzaldehyde (0.75 g; 5 mmole) in benzene

(30 ml) triethylamine (1.4 ml) and acetic anhydride (10 ml) were added.

The mixture was heated slowly to dissolve the solids and warmed below

reflux temperature for 10 min with a color change to dark brown. On

the evaporation of ca.. 15 ml of benzene a solid precipitated (0.2 g)

which was filtered and identified by ir as unreacted ylid. The filtrate

was heated an additional 5 minutes then evaporated to dryness. The

residue obtained was dissolved in ethanol (10 ml) and added to an

aqueous solution of sodium perchlorate (7 g; 20 ml). On the addition

of ether a light brown precipitate formed which filtered, washed with

ether but from which no pure product could be isolated.

Attempted Reaction of (Cyclopentadienylhydrazono)triphenyl-

phosphorane with Hydrobromic acid.- To a solution of 1 g of the ylid

in warm tetrahydrofuran (35 ml) was added 3.5 ml of 10% aqueous

hydrobromic acid. The clear solution was filtered into ether (100 ml).

An oil separated which would not crystallize on refrigeration. The

ether was decanted off and the remaining oil was dissolved in chloroform and dried over sodium sulfate. The oil obtained after filtration and removal of solvent in vacuo had in chloroform a band at 3400 cm$^{-1}$ (m) (broad; NH) but the resolution of the nmr spectrum was poor.

Trimethylammoniumcyclopentadienylide.- The method of Spooncer[38] was used for the preparation of this ylid with a few modifications.

Preparation of cis-3,5-Dibromocyclopentene in Petroleum Ether[91].- To a solution of 27.3 g (0.4 mole) of freshly distilled cyclopentadiene in 44 ml of petroleum ether (bp 35°-60°) maintained at -25° to -35°, was added over 45 minutes, with stirring, a solution of 64.1 g (0.4 mole) of bromine in 100 ml of petroleum ether. A semi-crystalline white precipitate appeared as the addition proceeded. Pyridine (2.7 ml) was added with stirring and the mixture was brought to 0°. A solution of 2.7 ml of acetic acid and 3.4 g of calcium chloride in 25 ml of water was added with stirring, and the mixture was brought to 0°. Two liquid phases resulted. The organic layer was separated and chilled 12 hr in a dry ice-acetone bath. The solid white crystalline mass was quickly transferred to a previously chilled Buchner funnel and filtered by suction. After most of the oily material has passed through but before discoloration of the remaining solid commenced, the slightly oily white solid was removed and rapidly recrystallized from petroleum ether (bp 66°-75°). This yielded 30 g (33.3%) of cis-3,5-dibromocyclopentene.

Trans-1,2-Bis-(dimethylamino)3-cyclopentene[77].- To a solution of 70 g (1.55 mole) of dimethylamine in 300 ml anhydrous benzene, cooled in an ice bath, 30 g of cis-3,5-dibromocyclopentene was added.

This mixture was allowed to stand at room temperature for 12 hr. The salt (30 g dimethylamine hydrobromide) was removed by filtration and the brown benzene solution was extracted with 400 ml of 15% hydrochloric acid. The layers were separated and the aqueous phase was made basic with solid potassium hydroxide (168.3 g; 3 mole), with cooling and stirring. The resulting brown solution was extracted a few times with ether. The ether was removed from the combined extracts and the resulting oil was made acidic with 2 N hydrochloric acid (300 ml) and heated 5 min. at 55-65° on a steam bath. The cooled acidic solution was extracted into 150 ml of ether and again made basic with potassium hydroxide (97.4 g). The ether solution from the three extractions with 150 ml of ether was dried over anhydrous sodium sulfate. After filtration and removal of solvent and distillation of the residue gave 11 g of amine bp 40-42°/1 mm.

Trans-1,2-Bis-(trimethylammonio)-3-cyclopentene diiodide[77].- To a solution of trans-1,2-bis-(dimethylamino)-3-cyclopentene (11 g, 71.4 mmol) dissolved in absolute ethanol (300 ml) methyl iodide (50.5 g; 0.356 mole) was added. The mixture was heated under reflux for 5 min. during which the salt separated as white crystals. After cooling, the dimethiodide (31.3 g; 90%) was collected, washed with cold ethanol and dried in air.

Trimethylammoniumcyclopentadienylide.- A 200 ml, three-necked flask was equipped with a mechanical stirrer, and an inlet tube for nitrogen which led directly into the reaction mixture. Into the flask at room temperature were then placed trans-1,2-bis-(trimethyl-ammonio)-3-cyclopentene diiodide (8.8 g; 0.02 mole) dissolved in water (20 ml). Stirring was started, nitrogen was bubbled through

the system and cold freshly prepared 40% potassium hydroxide (40 ml) solution was added. The flask was surrounded by a preheated oil bath (80-90°) and heated for 1 hr. Then the reaction mixture was allowed to cool to room temperature while the ylid precipitated as a pink crystalline solid. The product was collected, washed in sequence with cold 40% potassium hydroxide and ether. Final drying was accomplished by storage in a desiccator over phosphorus pentoxide. The desiccator was alternatively evacuated and filled with nitrogen several times, and left evacuated for two days before the system was opened. The ylid obtained (1.8 g; 75%) decomposed to a black solid on prolonged exposure to air.

Attempted Reaction of Trimethylammoniumcyclopentadienylide with Dimethylacetylenedicarboxylate.- Upon the addition of dimethylacetylenedicarboxylate (1.08 g) to the ylid (0.92 g) in chloroform (15 ml) an exothermic reaction took place. The mixture was left at room temperature for 12 hr. Removal of solvent in vacuo yielded an amorphous residue from which no identifiable product could be isolated.
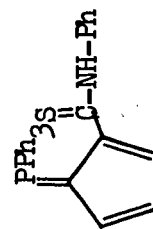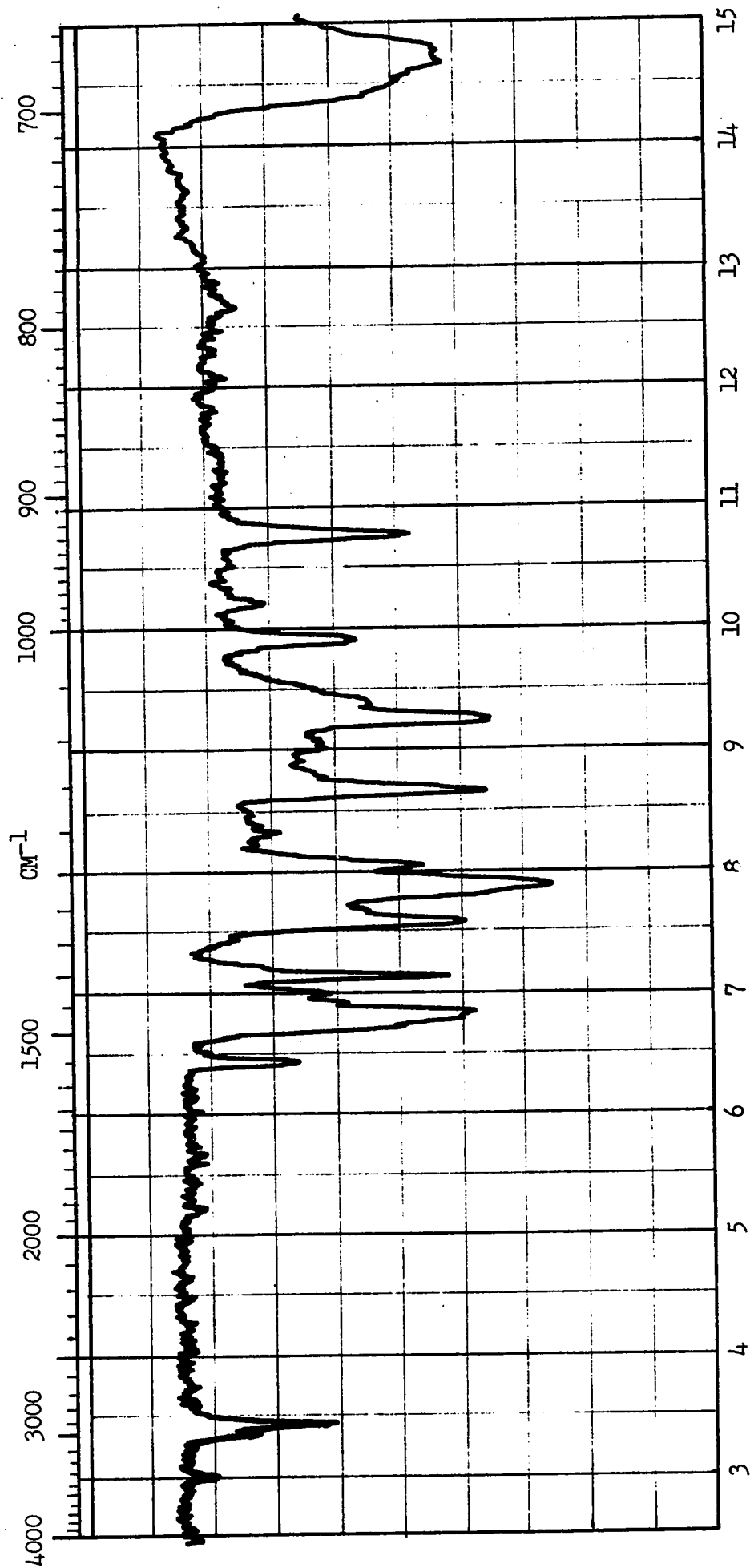
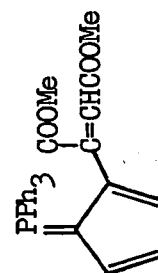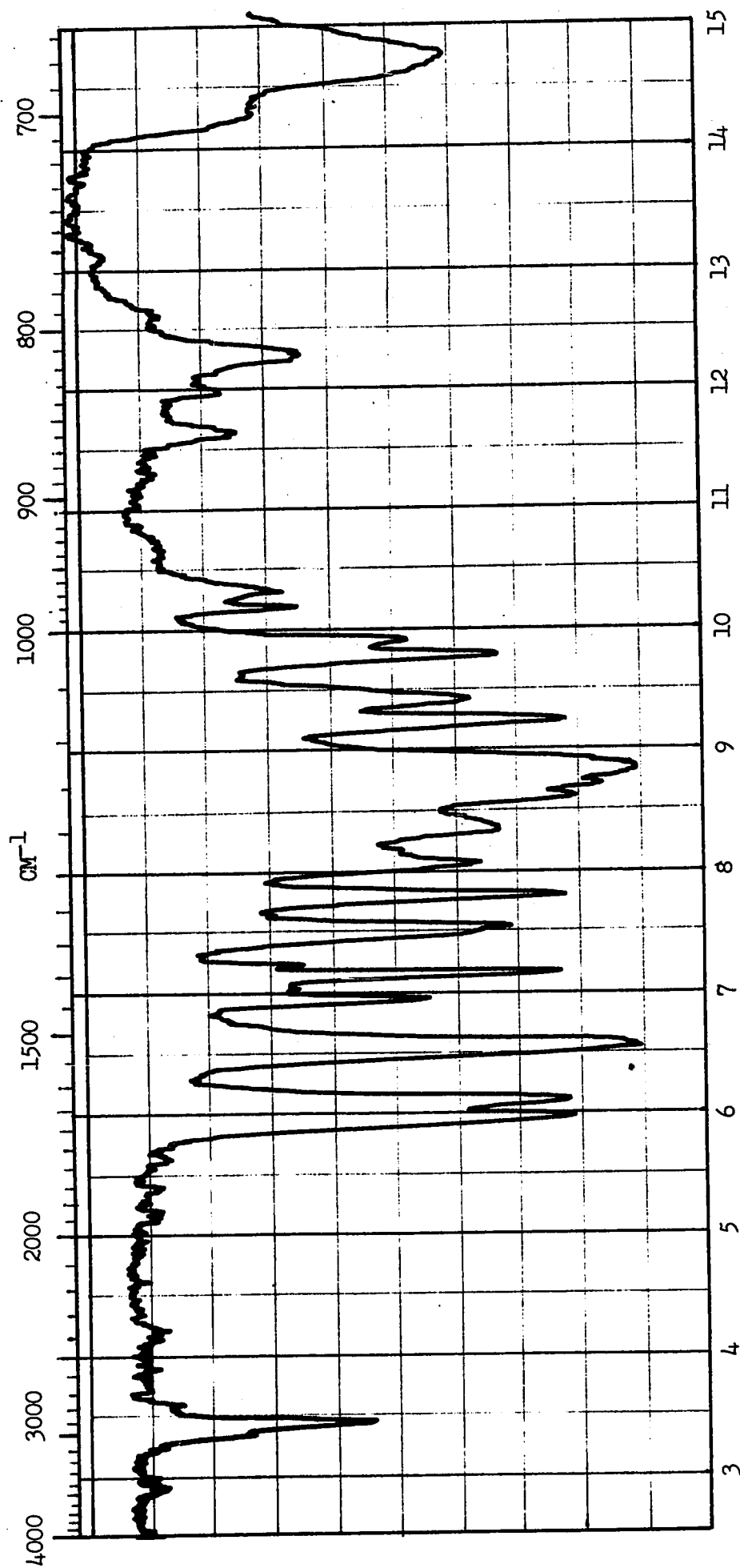APPENDIX

WAVELENGTH (MICRONS)
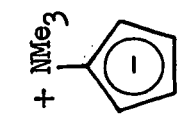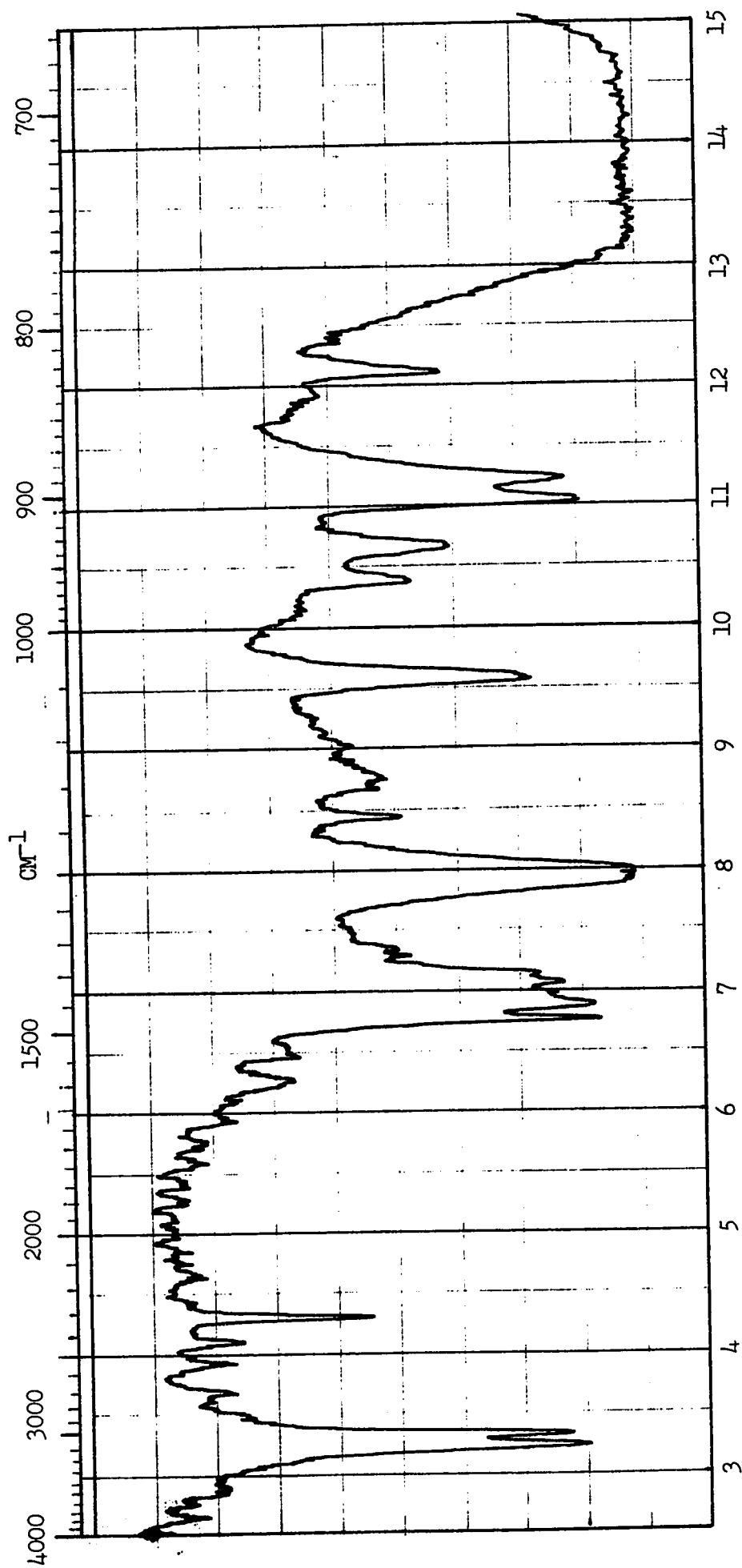
Infrared Spectrum No. 1

WAVELENGTH (MICRONS)

CM$^{-1}$
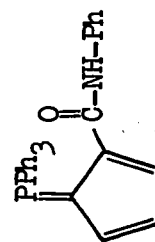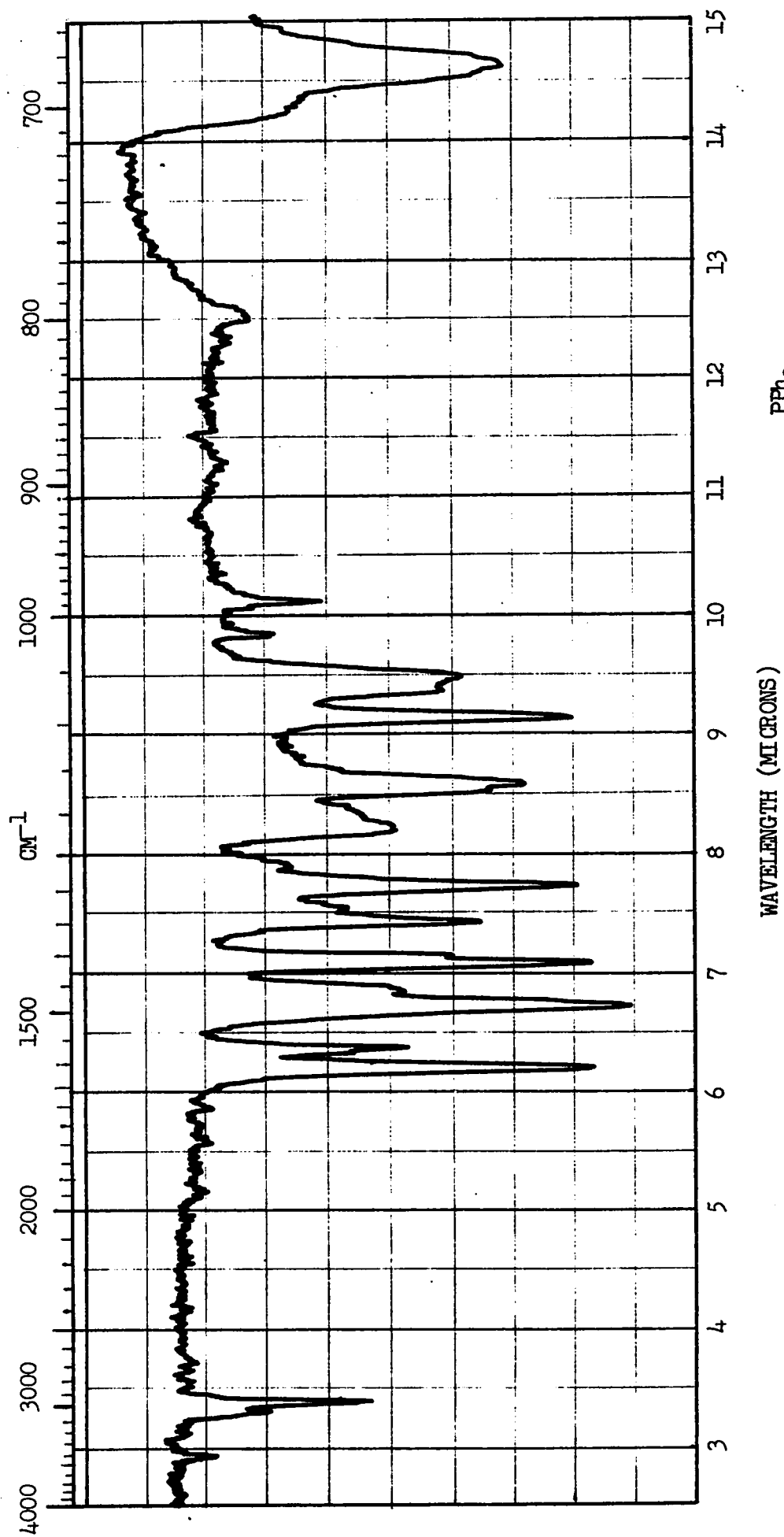
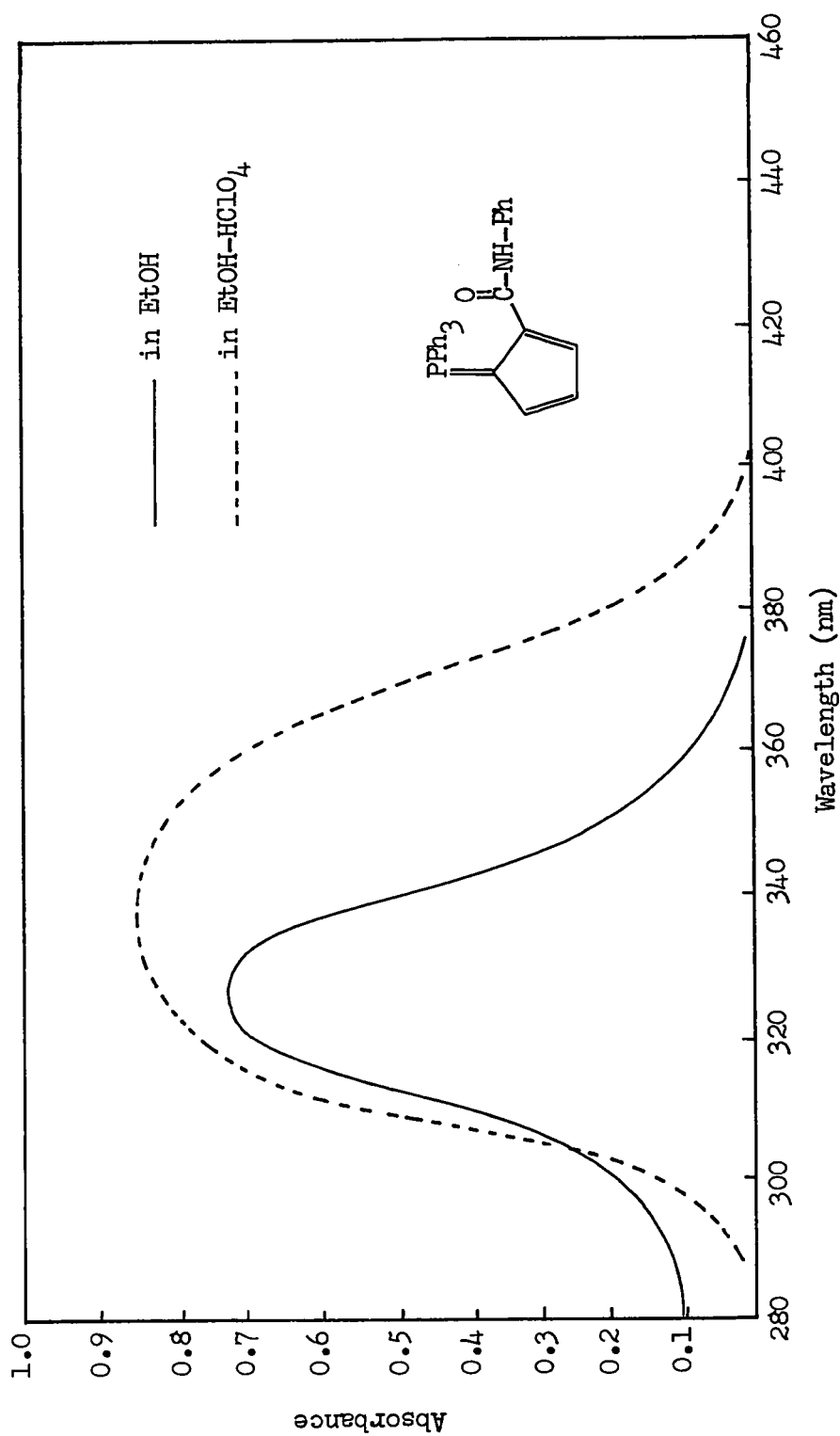Infrared Spectrum No. 2

83

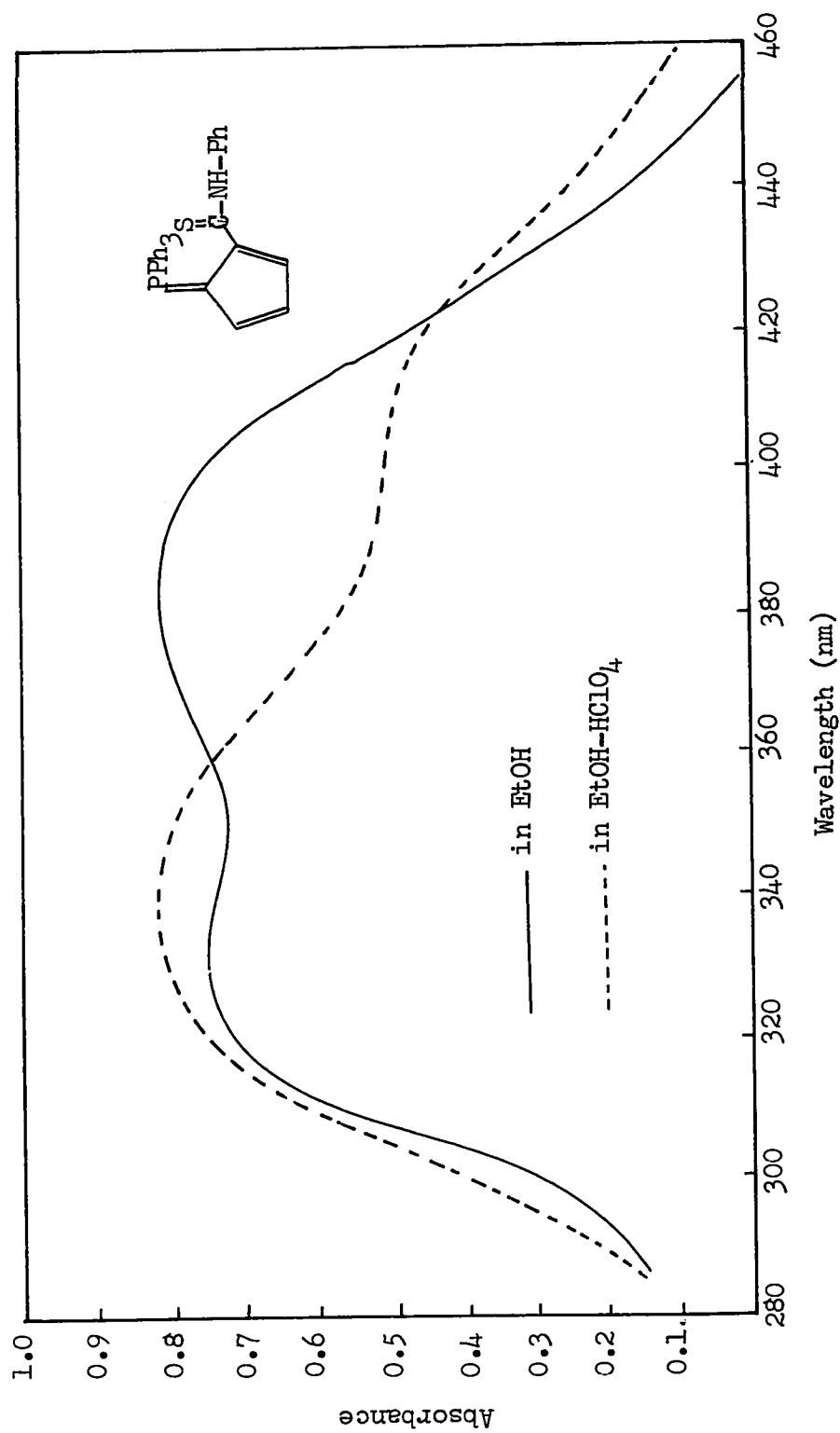WAVELENGTH (MICRONS)
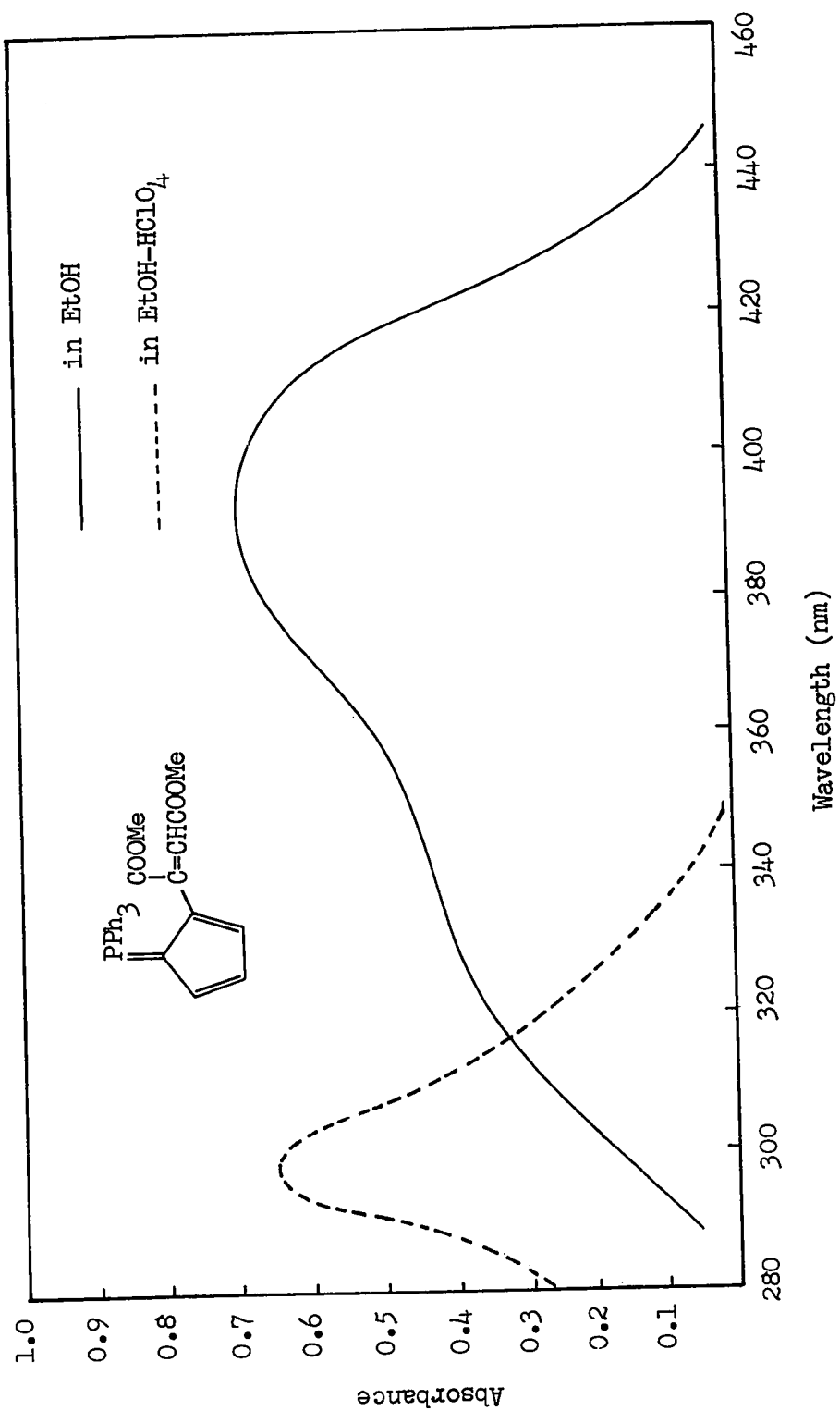
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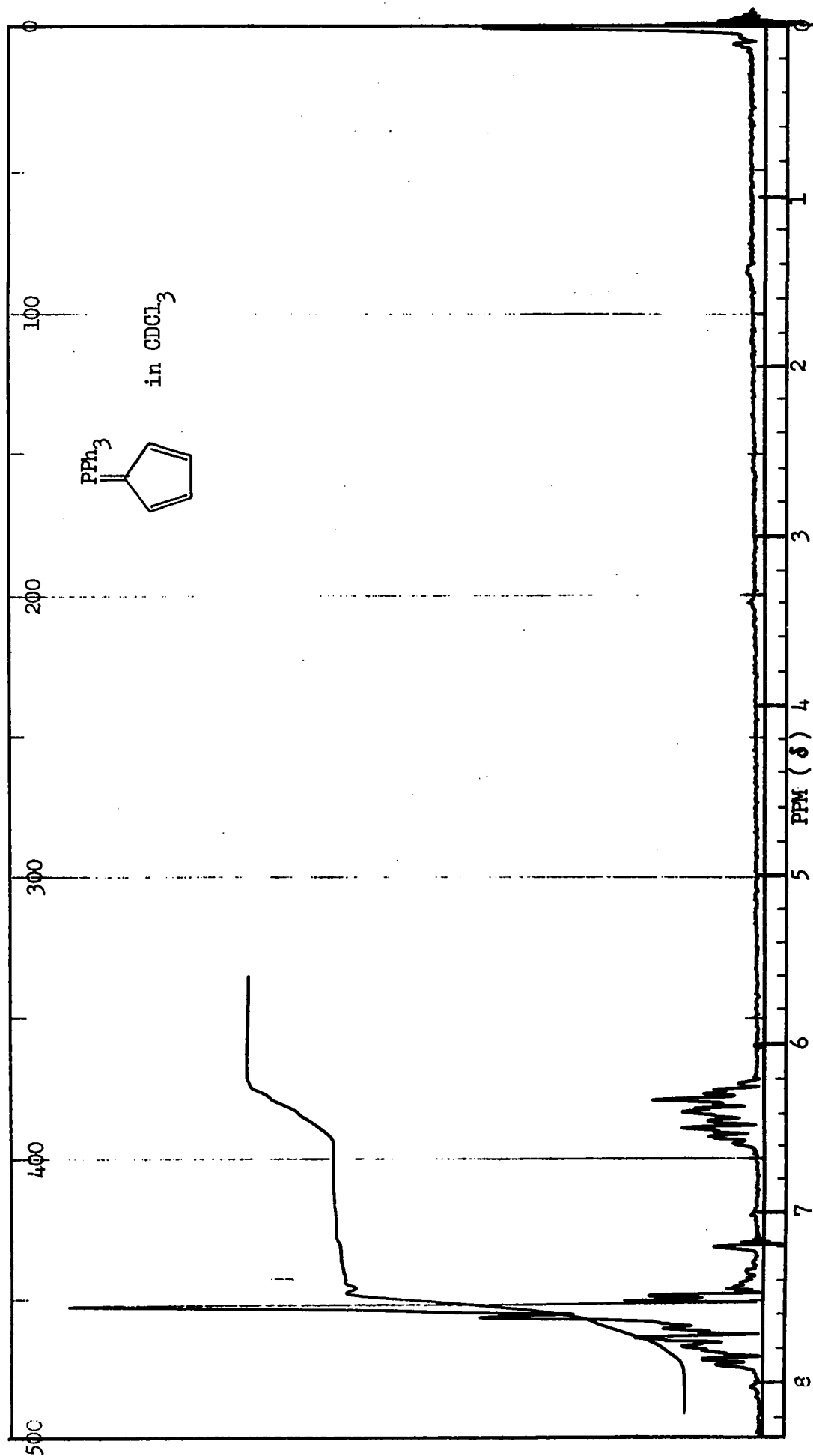WAVELENGTH (MICRONS)

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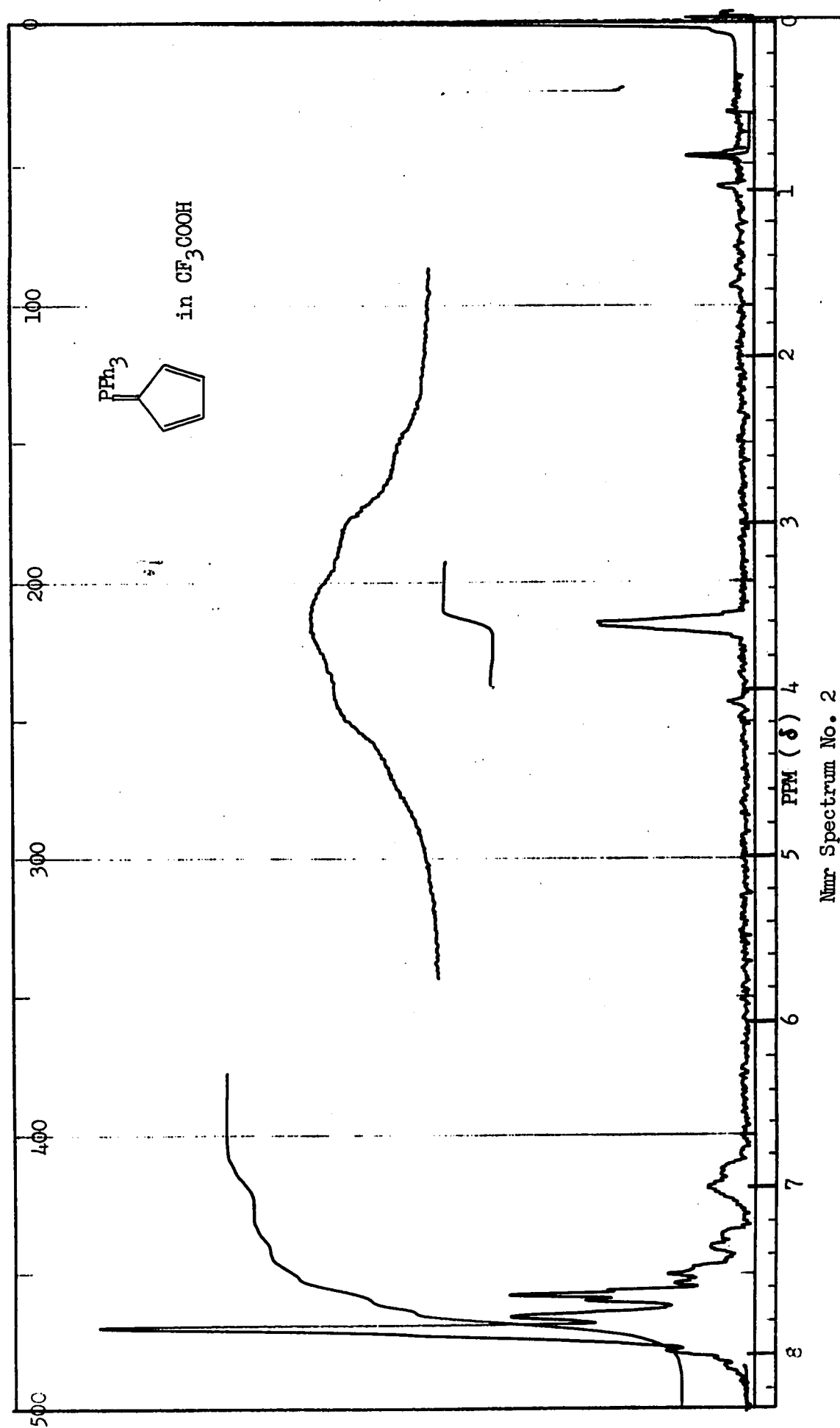
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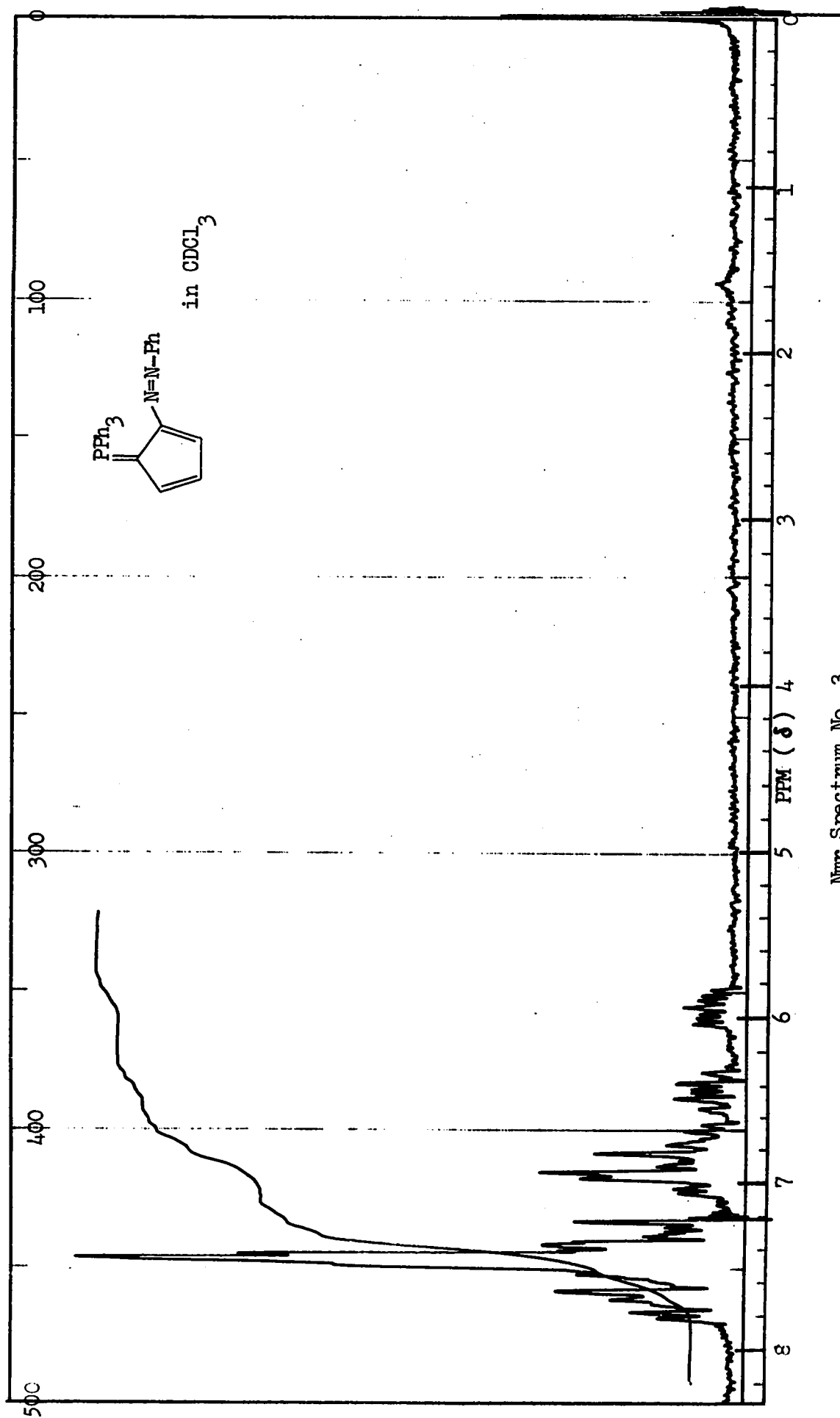Ultraviolet Spectrum No. 3
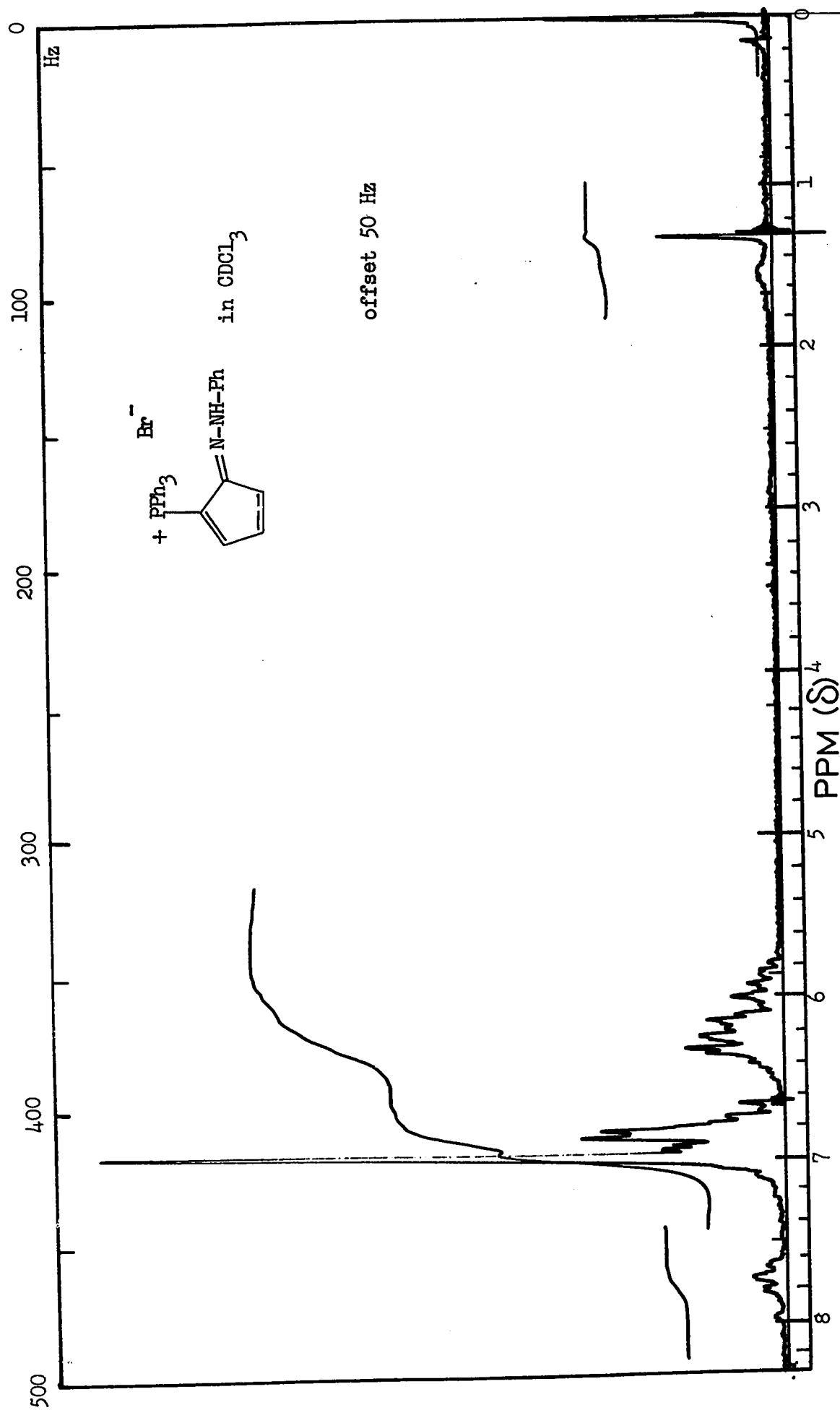
in CDCl₃

Nmr Spectrum No. 1

PPM ( δ )

in CF$_3$COOH

Nmr Spectrum No. 2

PPM ($\delta$)

in CDCl$_3$

Nmr Spectrum No. 3

PPM ($\delta$)

91

in CF$_3$COOH

offset 10 Hz

N=N–Ph

PPh$_3$

Hz

PPM ($\delta$)

Nmr Spectrum No. 4

Nmr Spectrum No. 5

in CDCl₃

Nmr Spectrum No. 6

94

in CF$_3$COOH

offset 100 Hz

Nmr Spectrum No. 7

96

PPh₃ S
|   ‖
C—NH—Ph

in CDCl₃

offset 300 Hz

Nmr Spectrum No. 8

in CF₃COOH

offset 100 Hz
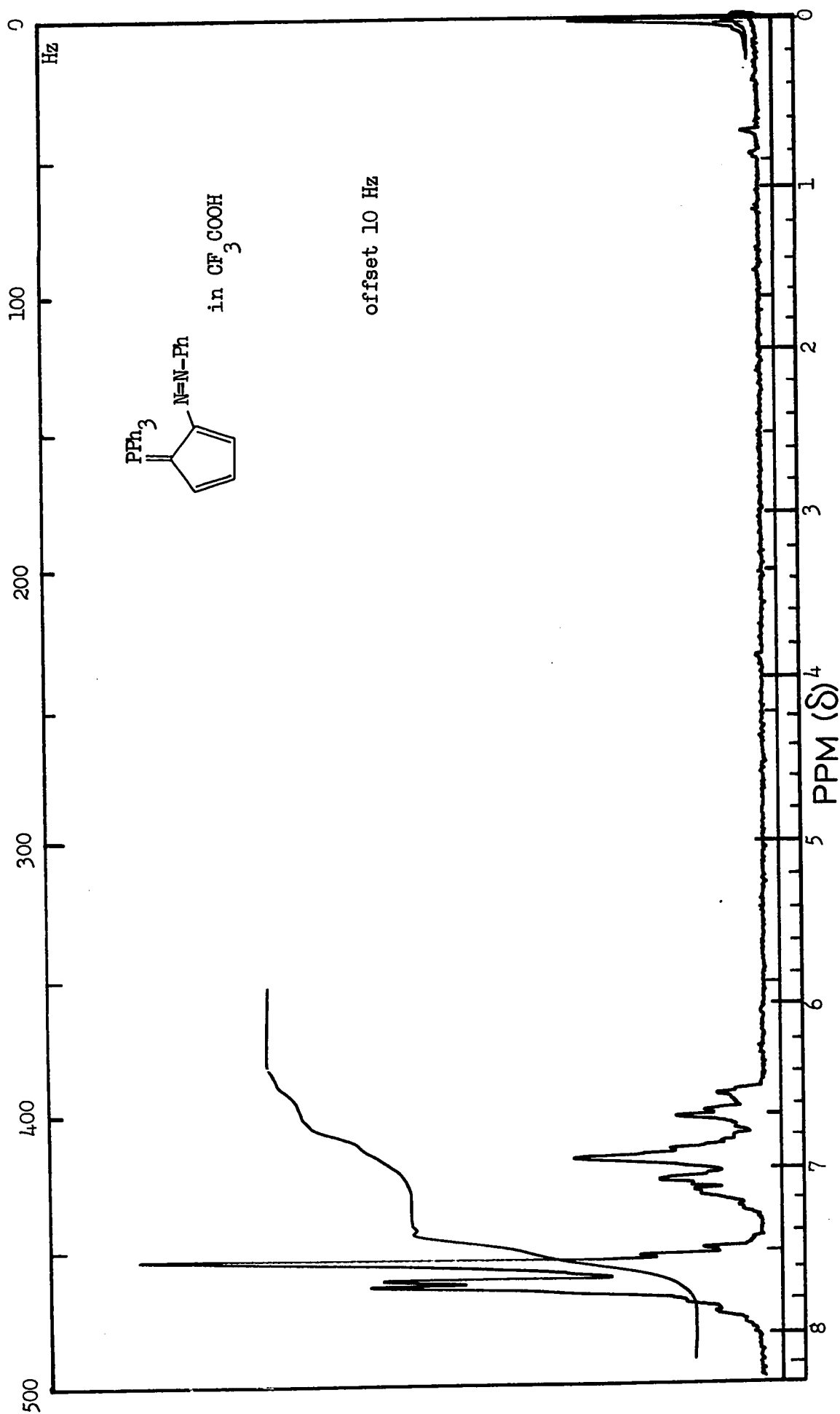
PPM ( δ )

Nmr Spectrum No. 9

in CDCl₃

Nmr Spectrum No. 10

in CF₃COOH

offset 100 Hz
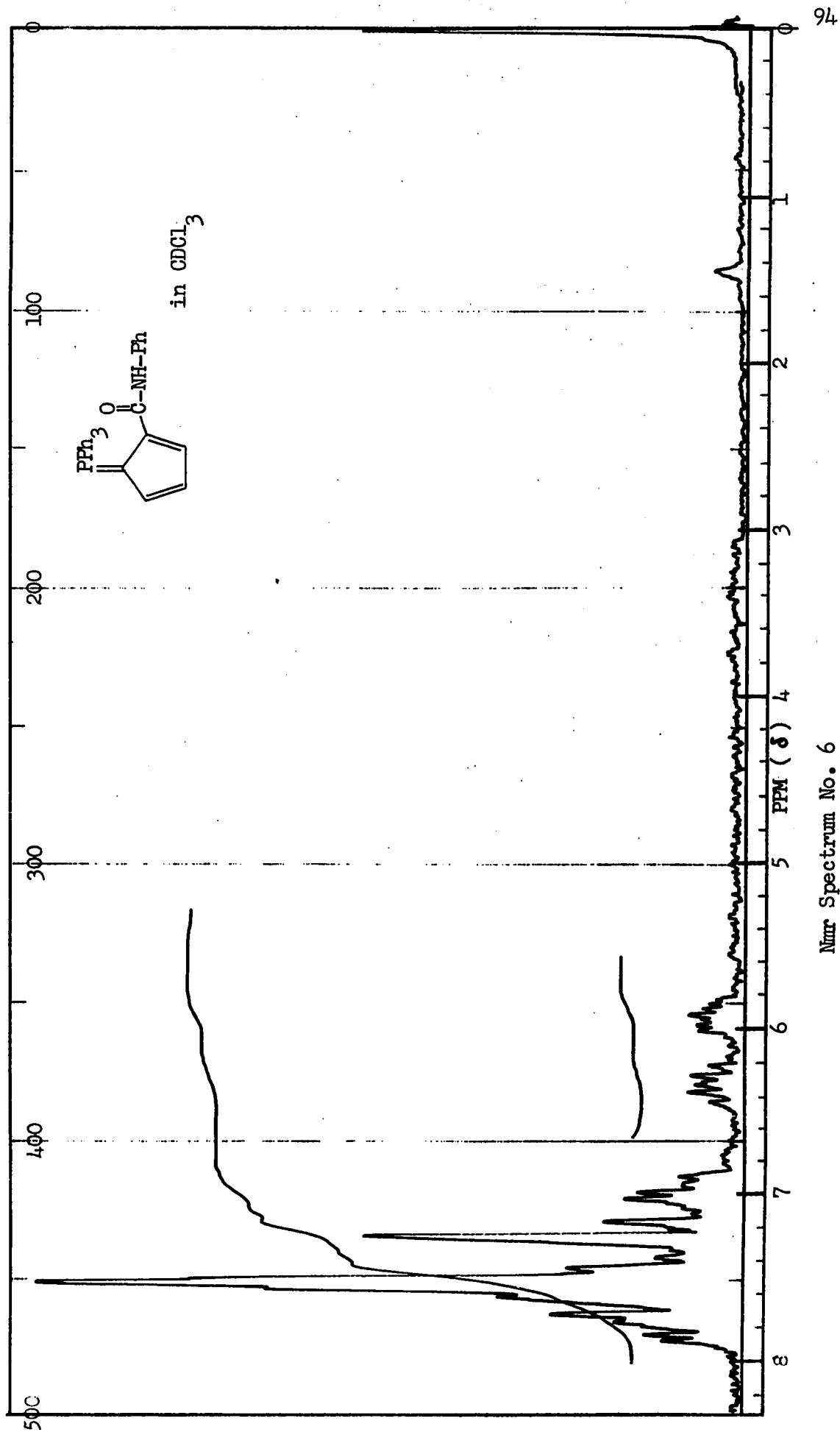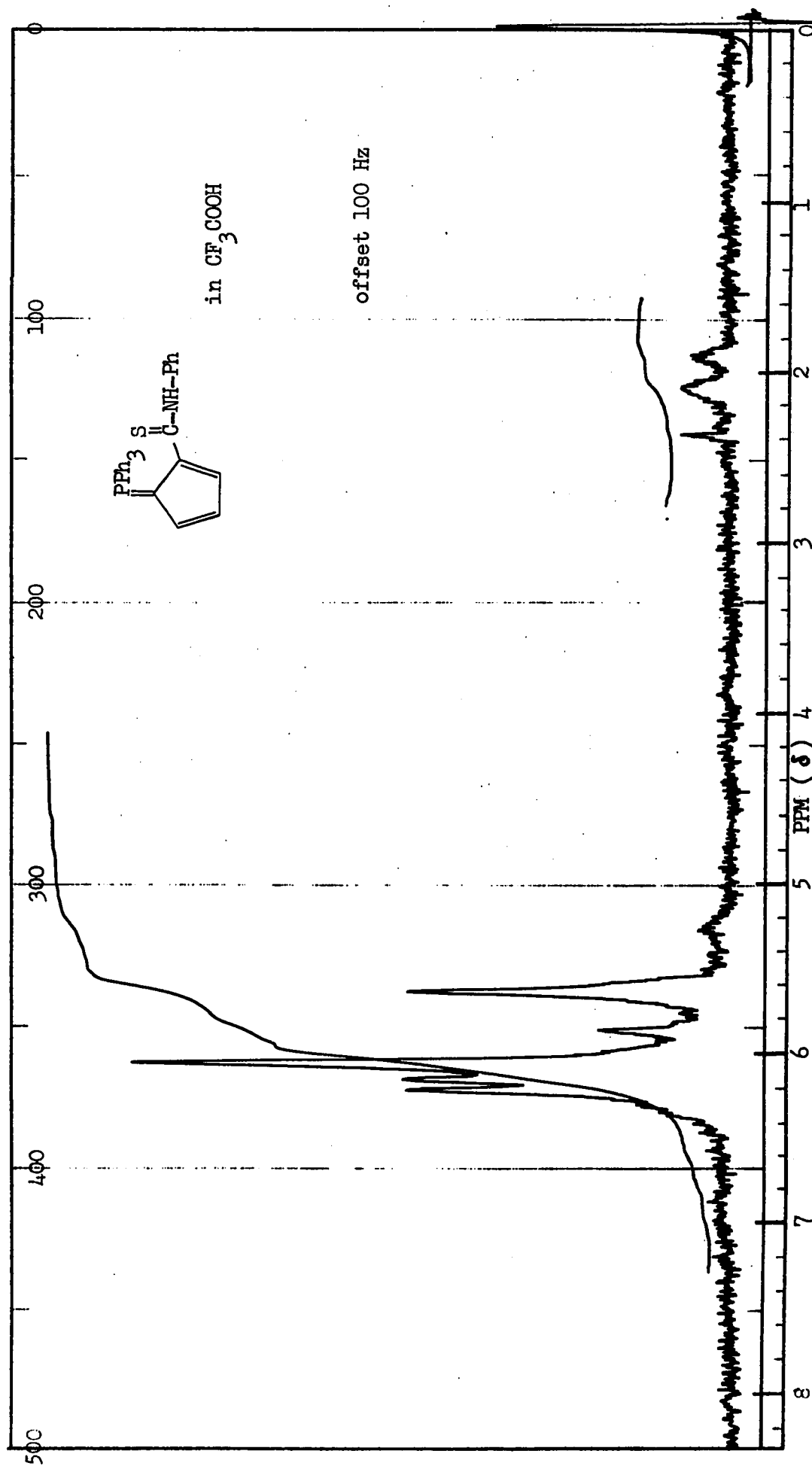
Nmr Spectrum No. 11

Nmr Spectrum No. 12

in CF$_3$COOH

+ NMe$_3$

offset
230 Hz

in CF$_3$COOH

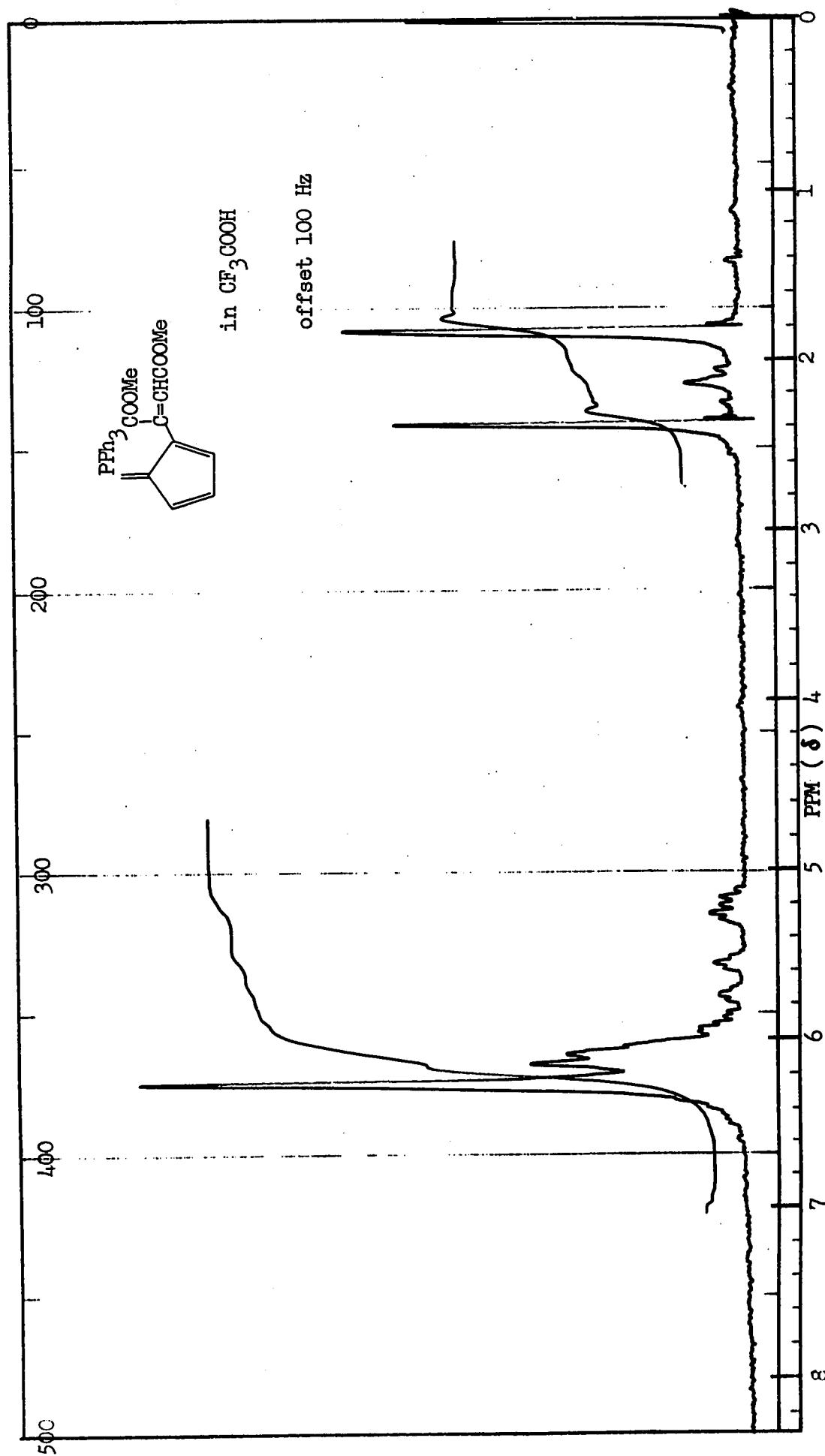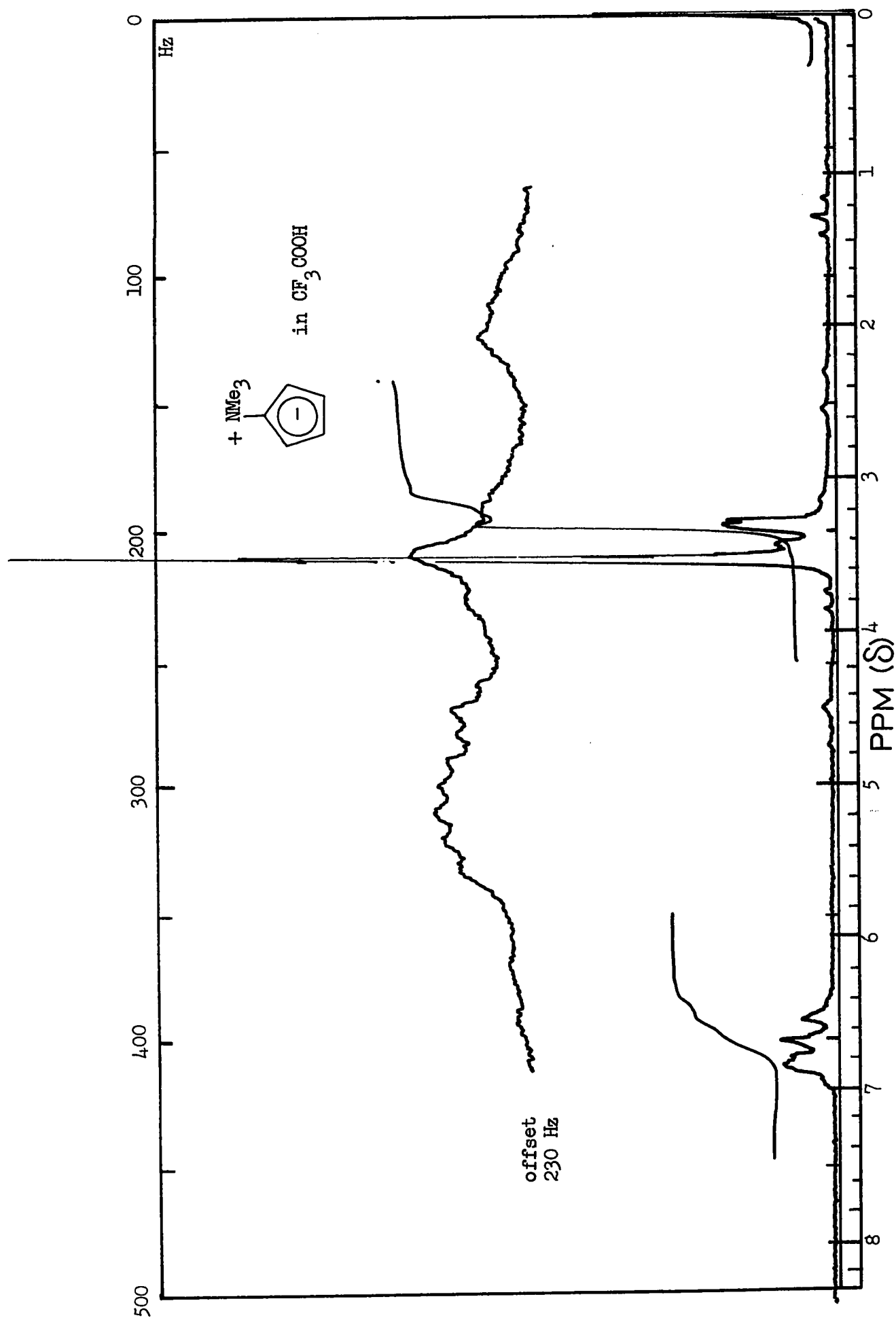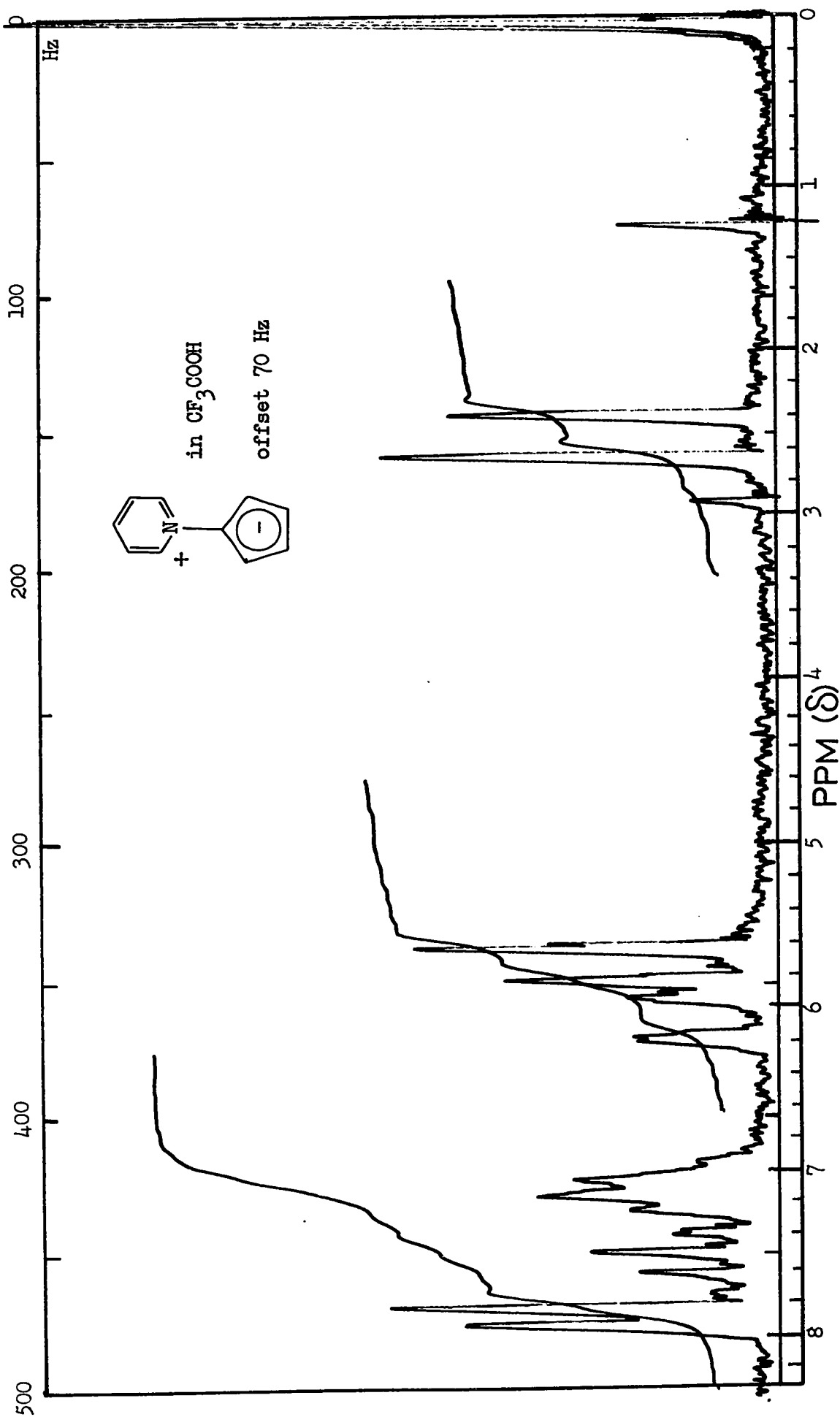offset 70 Hz
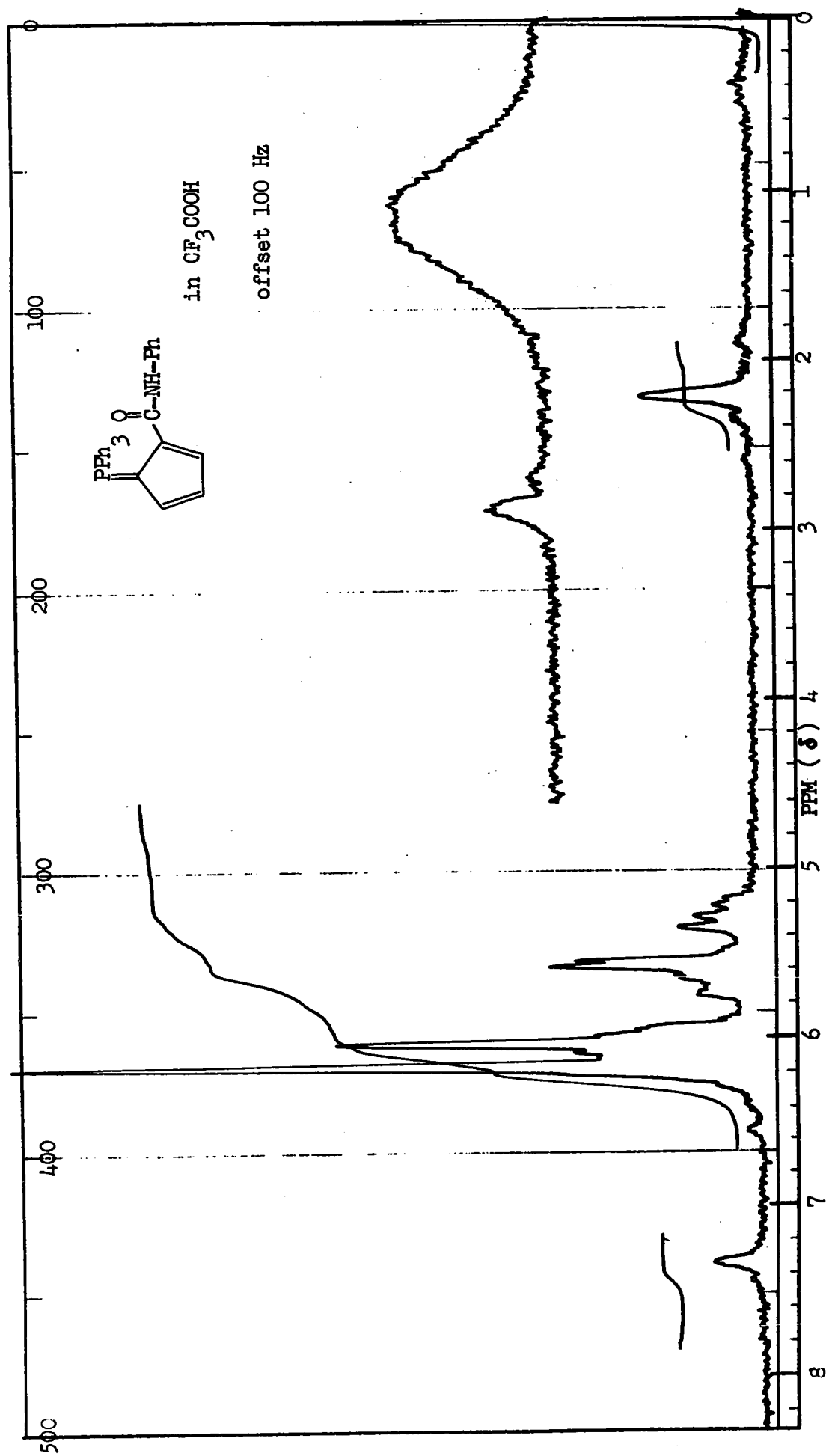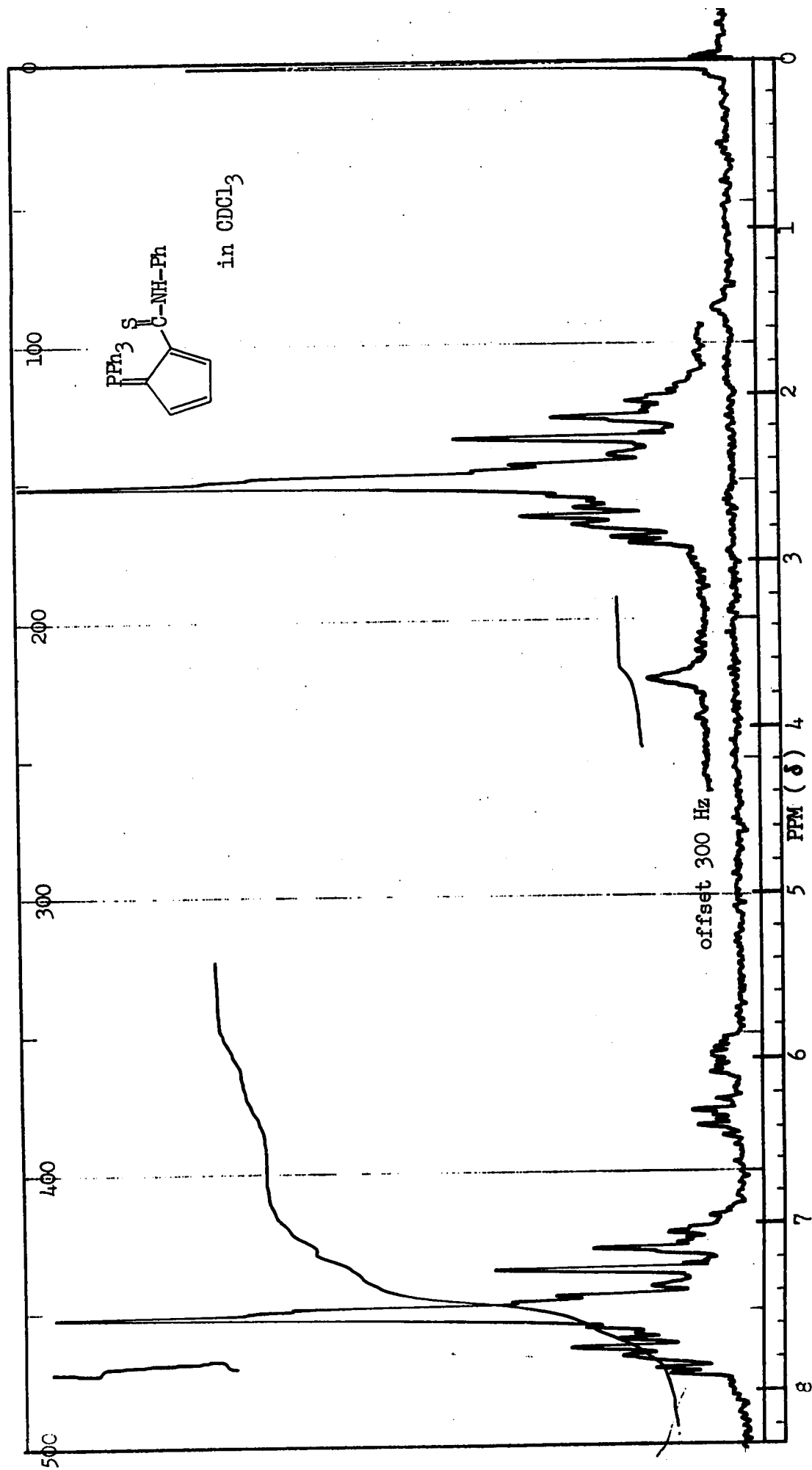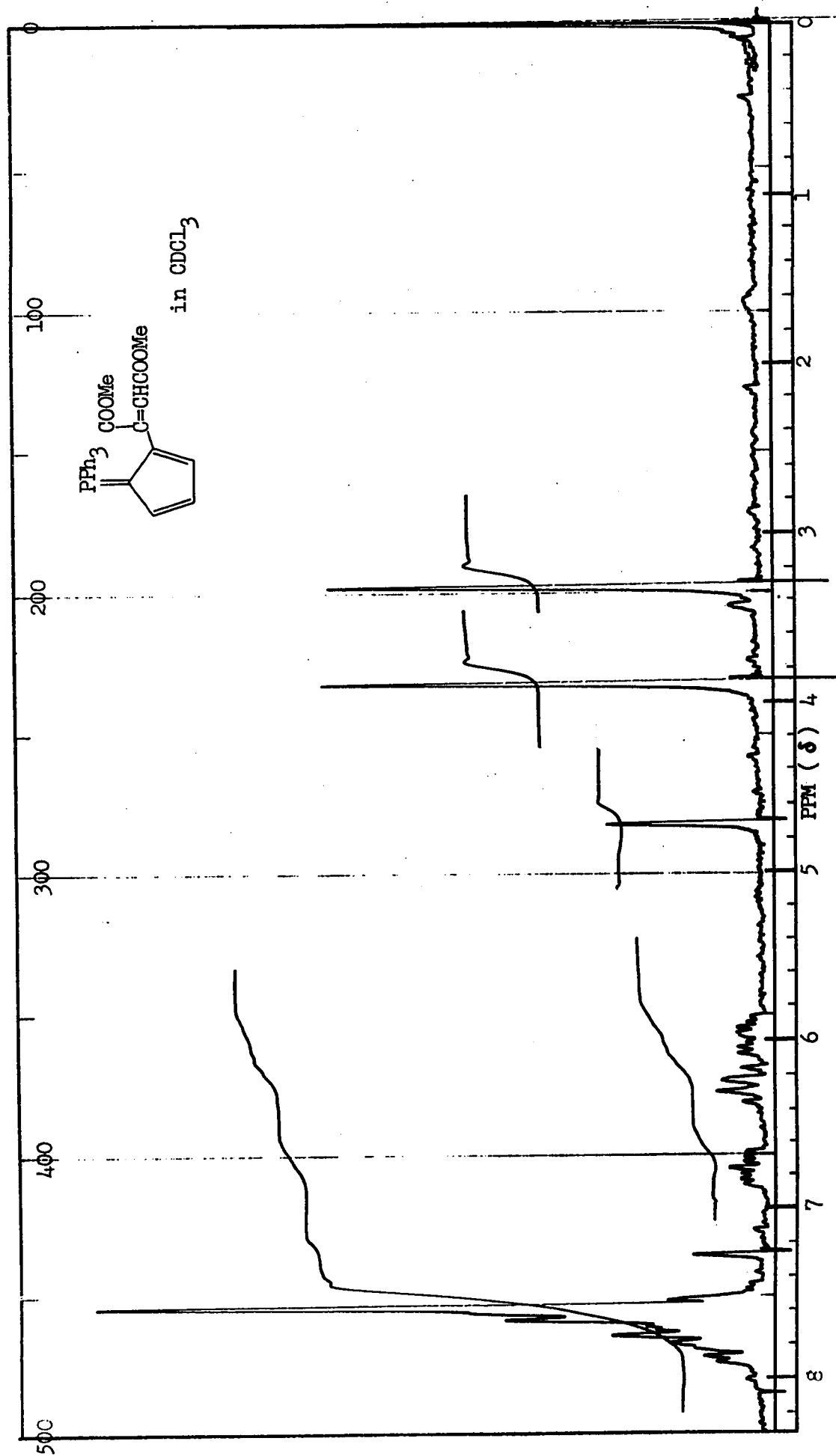
Nmr Spectrum No. 13

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