CYCLIZATIONS OF 1, 3-BISDIAZOPROPANE AND 3-DIAZOPROPENES

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This is to certify that the

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ABSTRACT

CYCLIZATIONS OF 1,3-BISDIAZOPROPANE AND 3-DIAZOPROPENES

by James Lee Brewbaker

The unstable bisdiazoalkane, 1,3-bisdiazopropane, was prepared from N,N'-trimethylenebis(N-nitrosobenzamide) by two methods. Treatment of solutions of this bisnitrosoamide in cyclohexene with methanolic sodium hydroxide produced the yellow diazo compound in 57% yield. When a solution of potassium ethoxide in ether was added to an ethereal solution of N,N'-trimethylenebis(N-nitrosobenzamide), potassium propane-1,3-bisdiazotate precipitated. This white solid was thermally stable but was decomposed by moisture. It reacted in methanol solution to form 1,3-bisdiazopropane in 49% yield.

At room temperature and in the dark the yellow color of a solution of 1,3-bisdiazopropane in cyclohexene slowly faded. A gas evolved and pyrazole was formed in 63% yield. The reaction does not involve the intermediate formation of 3-diazopropene, a compound which has been reported to cyclize to pyrazole (1,2). Pyrazole was formed from 1,3-bisdiazopropane at a greater rate than it was formed from 3-diazopropene under the same conditions.

The tautomerization of 3-diazopropene to pyrazole, which was first reported by Adamson and Kenner (1), is one example of a general reaction of β,γ-unsaturated diazoalkanes. Seven substituted 3-diazopropenes were prepared and all of these compounds readily cyclized to substituted pyrazoles. The rates of disappearance of these diazoalkenes were first order with respect to the diazoalkenes. The rates of cyclization of four substituted trans-3-diazo-1-phenylpropenes were only slightly altered by varying the substituents on the phenyl ring. When the substituent was p-methoxy, the rate was only 2.3 times larger than when the substituent was m-nitro. These data fitted the Hammett equation correlating well with σ constants. The ρ value for the reaction in cyclohexene at 25° was -0.40. The lack of sensitivity of the cyclization rate to the electronic nature of substituents suggested that the reaction occurred by a synchronous, cyclic shift of electrons in which charge distribution in the transition state was not markedly different from that in the ground state.

The 3-diazopropenes were prepared by treating the appropriate ethyl alkenylnitrosocarbamates with methanolic sodium methoxide. The yield of diazoalkene depended on the nature of the alkenyl group. Structural features which stabilize negative charge favored the formation of high yields of diazo compound; those features which stabilize positive charge led to lower yields of diazo compound.

In addition to diazo compound, allylic ethers were also formed. For example, ethyl allylnitrosocarbamate yielded both 3-diazopropene and allyl methyl ether. Under the preparative conditions the diazoalkenes and methanol did not react. Thus, ethers were not formed by further reaction of these diazoalkenes but were produced by a process that was competitive with the one leading to the diazo compounds.

The ratios of _trans_-1-methoxy-2-butene to 3-methoxy-1-butene produced by the reactions of ethyl _trans_-2-butenylnitrosocarbamate and ethyl 1-methyl-2-propenylnitrosocarbamate with methanolic sodium methoxide were 3.6 and 0.48 respectively. If these ethers were formed from the free butenyl carbonium ion, the ratios produced from the two isomeric nitrosocarbamates would have been the same. They were not. Therefore, the major reaction path leading to solvolysis products did not involve a free carbonium ion.

REFERENCES

1. D. W. Adamson and J. Kenner, J. Chem. Soc., 286 (1935).
2. C. W. Hurd and S. C. Lui, J. Am. Chem. Soc., _57_, 2656 (1935).

CYCLIZATIONS OF 1,3-BISDIAZOPROPANE AND 3-DIAZOPROPENES

By

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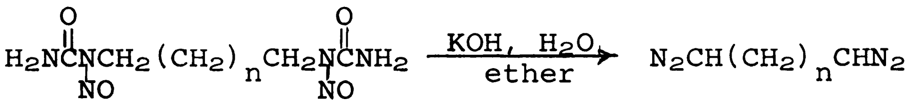
I. INTRODUCTION

In 1883 Curtius reported the preparation of the first known alipahtic diazo compound, ethyl diazoacetate (1). Eleven years later von Pechman (2) established the structure of diazomethane after careful study of the yellow gas which had been discovered four years earlier (3). Since then diazoalkanes, especially diazomethane, have become commonly used reagents in organic synthesis (4,5,6). The great variety of their reactions has held the interest of chemists for many years.

In this thesis we have reported the results of investigations of two types of diazoalkanes, an α,ω-bisdiazoalkane and several β,γ-unsaturated diazoalkanes. These compounds were observed to cyclize to pyrazoles spontaneously at room temperature. The purposes of this investigation were to test the generality of this cyclization and to elucidate the mechanism by which it occurred.

Unlike diazoalkanes, bisdiazoalkanes have not been extensively studied. In 1949 Lettre and Brose prepared the series of bisdiazoalkanes 2c, 2d and 2e by treating ethereal solutions of the corresponding N,N'-dinitrosoureas (1c, 1d and 1e) with aqueous potassium hydroxide (7).



$$H_2N\overset{O}{\overset{\|}{C}}\underset{NO}{N}CH_2(CH_2)_nCH_2\underset{NO}{N}\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow[\text{ether}]{KOH,\ H_2O} N_2CH(CH_2)_nCHN_2$$

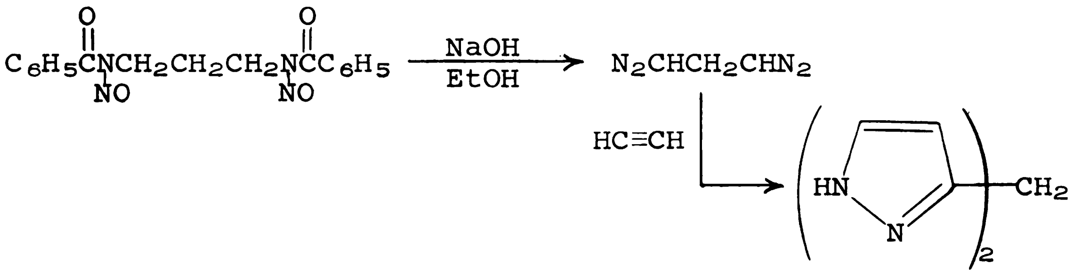
1 2

a n=0 c n=2 e n=4

b n=1 d n=3 f n=5

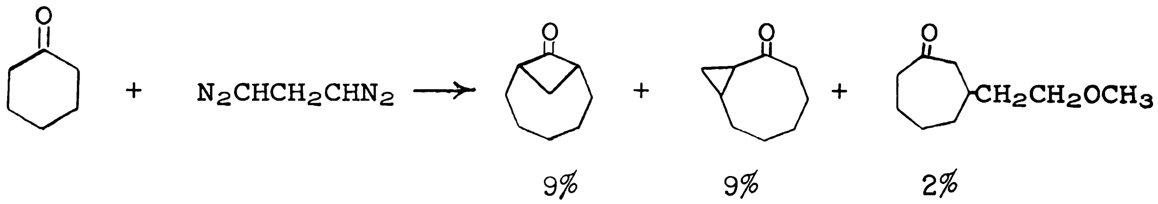
They found this procedure acceptable for the preparation of <u>2c</u>, <u>2d</u>, and <u>2e</u> but observed that when they tried to prepare 1,3-bisdiazopropane (<u>2b</u>), numerous side reactions occurred and only a small amount of the yellow bisdiazo compound was extracted into the ether layer. Lieser and Beck (8) also reported the preparation of this series of compounds (<u>2a-2f</u>) using essentially the same procedure as employed by Lettre and Brose. They noted that α,ω-bisdiazoalkanes are highly unstable and that their stability decreases as the number of carbon atoms between the two diazo groups decreases.

H. Reimlinger prepared 1,3-bisdiazopropane from N,N'-trimethylenebis(N-nitrosobenzamide) (<u>3</u>) in a mixed solvent of ethanol and ether by adding ethanolic sodium hydroxide (9). The yield was not reported but the author did state that 1,3-bisdiazopropane and acetylene react to form bis[pyrazolyl-3-]methane (<u>4</u>) in a yield of 85%.



<u>3</u> <u>4</u>

Cyclohexanone and 1,3-bisdiazopropane react to form the bicyclic ketones and keto ether shown below (10).



The 1,3-bisdiazopropane was generated in situ by stirring the corresponding N-nitrosourea (1b) and potassium carbonate in cyclohexanone.

Solid derivatives of 1,3-bisdiazopropane have been prepared by treating the diazo compound with benzoic acid or p-nitrobenzoic acid. The products of these reactions are the corresponding diesters of 1,3-propanediol. Phenol and 1,3-bisdiazopropane react to form the diphenyl ether of 1,3-propanediol (8). The yields for these last three reactions were not reported.

The cyclization of β,γ-unsaturated diazo compounds is not a new reaction. It has been mentioned briefly before. In 1935 Hurd and Lui (11) prepared 3-diazopropene by treating an ether solution of ethyl allylnitrosocarbamate with aqueous potassium hydroxide. In the same year Adamson and Kenner (12) prepared 3-diazopropene from N-allyl-N-nitroso-4-amino-4-methyl-2-pentanone and sodium isopropoxide. Both groups of researchers noted that the compound slowly changed to pyrazole when its ether solutions were allowed to stand at room temperature. No yields were reported. Adamson and Kenner observed that the rate at which the color of an ether solution of 3-diazopropene faded was sensitive to light (12).

While the present work was in progress Ledwith and Parry reported on the light sensitivity of this reaction in more detail (13). The photo reaction is about three times faster than the thermal reaction at 25° although its rate appears to be independent of the intensity of irradiation at all but very low light levels. The thermal reaction follows first order kinetics.

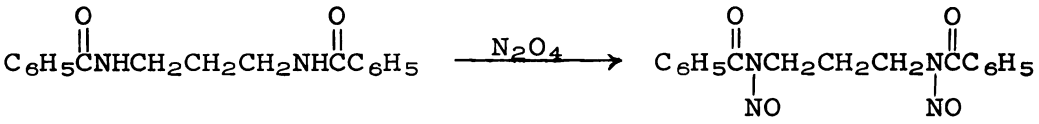
The cyclization of _trans_-1-diazo-2-butene to 3(5)-methylpyrazole is the only other reported example of the cyclization of a β,γ-unsaturated diazoalkane. Adamson and Kenner (12) observed that the color of an ether solution of _trans_-1-diazo-2-butene slowly faded at room temperature; however, they did not identify the product of the reaction. Later Curtin and Gerber (14) identified the product as 3(5)-methylpyrazole. Again no yield was reported.

In the following sections of this thesis the results of a study of 1,3-bisdiazopropane and of eight substituted 3-diazopropenes are reported. Their preparations and their thermal decompositions to produce pyrazoles are described. A comparison of the rates at which these diazo compounds cyclize contributes to an understanding of the mechanism by which the cyclization occurs. This comparison is included in the discussion. The 3-diazopropenes were prepared by treating the corresponding ethyl alkenylnitrosocarbamates with methanolic sodium methoxide. In addition to the diazoalkenes, products that can be rationalized as arising from the alkenyl carbonium ions were also formed. The relative yields of these products were dependent on the nature of the alkenyl group. This dependency is also discussed.

II. RESULTS AND DISCUSSION

A. 1,3-Bisdiazopropane

1. Preparation. Cyclohexene solutions of 1,3-bisdiazopropane were prepared by two methods. The precursor for both of these preparations was N,N'-trimethylenebis(N-nitrosobenzamide) (6), the material from which Reimlinger (9) previously prepared 1,3-bisdiazopropane. N,N'-Trimethylenebis(N-nitrosobenzamide) is a stable, yellow solid which was prepared in high yield by adding dinitrogen tetroxide to a cold solution of N,N'-trimethylenebisbenzamide (5) in 1:1 acetic acid-acetic anhydride.

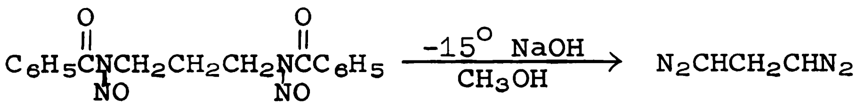


$$\mathrm{C_6H_5\overset{O}{\overset{\|}{C}}NHCH_2CH_2CH_2NH\overset{O}{\overset{\|}{C}}C_6H_5} \xrightarrow{\mathrm{N_2O_4}} \mathrm{C_6H_5\overset{O}{\overset{\|}{C}}\underset{NO}{N}CH_2CH_2CH_2\underset{NO}{N}\overset{O}{\overset{\|}{C}}C_6H_5}$$

5 6 97%

This compound was stored in a refrigerator for a year without noticeable change although at room temperature and in room light some decomposition occurred after two months.

A clear, yellow solution of 1,3-bisdiazopropane in cyclohexene was prepared by stirring a solution of 6 in cyclohexene with methanolic sodium hydroxide for 4 hr at -15°.



$$\mathrm{C_6H_5\overset{O}{\overset{\|}{C}}\underset{NO}{N}CH_2CH_2CH_2\underset{NO}{N}\overset{O}{\overset{\|}{C}}C_6H_5} \xrightarrow[\mathrm{CH_3OH}]{-15^{\circ}\ \mathrm{NaOH}} \mathrm{N_2CHCH_2CHN_2}$$

6 57%

The yield of 1,3-bisdiazopropane was 57%. The system used had two liquid phases. 1,3-Bisdiazopropane was generated in the lower, methanolic phase and was extracted into the upper, cyclohexene layer. The layers were separated, and the cyclohexene layer was quickly extracted with cold 10% aqueous base to remove the dissolved methanol. The resulting clear, yellow solution was dried over potassium hydroxide pellets at -15^{o}. Dry solutions of 1,3-bisdiazopropane in cyclohexene are stable at -15^{o}. At 0^{o} a very slow evolution of gas can be seen and at 25^{o} the compound has a half life of about 2 hr. Reimlinger (9) isolated several α,ω-bisdiazoalkanes at -70^{o}. He reported that these yellow oils decomposed explosively when warmed to room temperature. Because of the potential danger in handling pure 1,3-bisdiazopropane, we made no attempt to isolate the compound. All our work was done using dilute solutions of 1,3-bisdiazopropane. No explosions occurred.

The procedure for the preparation of 1,3-bisdiazopropane described above is very similar to the procedure described briefly by Reimlinger (9) for the preparation of the same compound. The only major difference is the solvent. Reimlinger used a mixture of ethanol and ether; we used cyclohexene and methanol. We had originally planned to study the photolytic reaction of 1,3-disdiazopropane and cyclohexene. This was the reason for our choice of solvent. However, the photolysis of 1,3-bisdiazopropane in cyclohexene did not give clean results and as a result, that aspect of the project was abandoned and a study of the thermal decomposition of

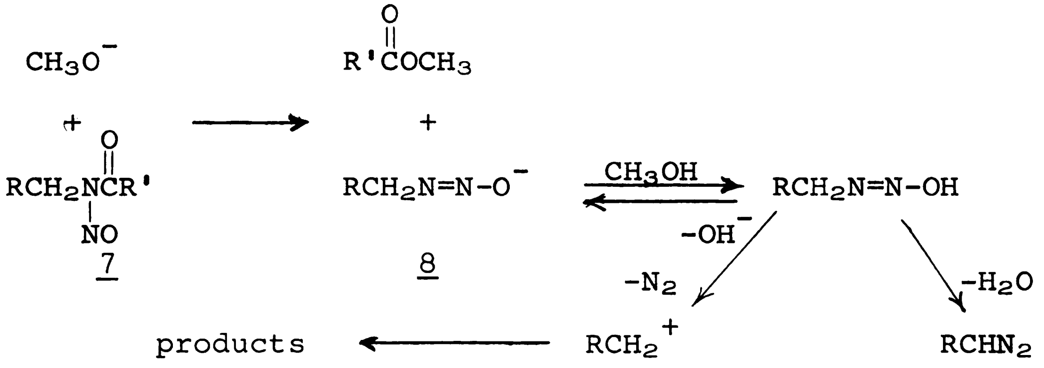
1,3-bisdiazopropane was initiated. Since the procedure for generating 1,3-bisdiazopropane in cyclohexene had already been developed, this solvent was used throughout the remainder of the investigation. Whether our method of preparing 1,3-bisdiazopropane is any better than the one reported by Reimlinger is not clear. Reimlinger did not describe his procedure in detail and did not report a yield.

The infrared spectra of solutions of 1,3-bisdiazopropane prepared as described above showed two intense bands at 2065 and 1721 cm^{-1}. The former band is characteristic of the diazo group (15) and the latter is due to methyl benzoate. Methyl benzoate was produced by attack of methoxide anion on the carbonyl carbon of N,N'-trimethylenebis(N-nitrosobenzamide) and is a co-product of the reaction. Its presence in the solution sometimes complicated the isolation of products of reactions in which 1,3-bisdiazopropane was employed as a reactant.

A second method of preparing 1,3-bisdiazopropane, which was developed during our investigation, avoided this difficulty by yielding solutions of the diazo compound that were free of methyl benzoate. This method involved isolation of the intermediate, potassium propane-1,3-bisdiazotate.

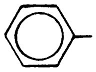
Previous workers have shown that the production of diazo compounds by treatment of N-nitrosoamides (7) with alkoxide involves initial attack of the alkoxide anion on the carbonyl carbon of the nitrosoamide (16,17) forming a diazotate (8) (16).

In protic solvents the diazotate reacts further producing either diazoalkane (9) or solvolysis products (4,16,18,19, 20,21).

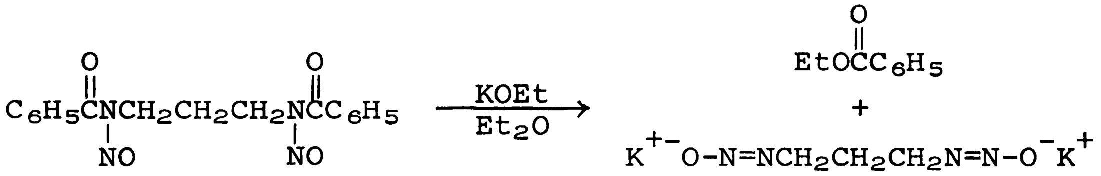


The relative amounts of diazoalkane and solvolysis products produced are highly dependent on the nature of R (20) and also on the basicity of the medium in which the reaction is carried out. Moss reported that cyclohexyl diazotate (8, R = $-(CH_2)_5-$) is decomposed by water to produce only cyclohexene and cyclohexanol whereas in methanol diazocyclohexane is also produced (20). Early workers believed that solvolysis products were the result of decomposition of the diazoalkane but recently obtained evidence shows that the formation of diazoalkane and solvolysis products are competitive processes and that the diazotate (or diazonium hydroxide) is the common intermediate (19,20).

Diazotates may be isolated as thermally stable, white salts which are very sensitive to moisture. However, until two years ago, only two such compounds were reported in the literature. Hantzsch and Lehmann (22) prepared both potassium methyldiazotate (23) (8, R=H) and potassium benzyldiazotate

(8, R= ) by treating ethyl methylnitrosocarbamate and ethyl benzylnitrosocarbamate with very concentrated aqueous potassium hydroxide solutions. Recently seven other diazotates have been reported (20,24).

We found that when a solution of N,N'-trimethylenebis-(N-nitrosobenzamide) in anhydrous ether was added to a solution of potassium ethoxide in ether, potassium propane-1,3-bisdiazotate (10) immediately precipitated.



$$\underset{\textstyle \underline{6}}{C_6H_5\overset{O}{\overset{\|}{C}}\underset{NO}{\underset{|}{N}}CH_2CH_2CH_2\underset{NO}{\underset{|}{N}}\overset{O}{\overset{\|}{C}}C_6H_5} \xrightarrow[Et_2O]{KOEt} \begin{matrix} EtO\overset{O}{\overset{\|}{C}}C_6H_5 \\ + \\ \underset{\textstyle \underline{10}}{K^{+}\,{}^{-}O\text{-}N{=}NCH_2CH_2CH_2N{=}N\text{-}O^{-}\,K^{+}} \end{matrix}$$

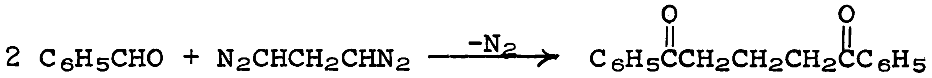
This white solid was insoluble in common organic solvents and was stable at room temperature when stored under dry nitrogen. It decomposed evolving a gas when brought into contact with protic solvents such as water or methyl alcohol. The rate of gas evolution was markedly dependent on the acidity of the medium. Decomposition was very slow in 50% aqueous potassium hydroxide solution but gas evolved violently when the material was added to 1 N aqueous sulfuric acid. Ethyl benzoate was also a product of the reaction. In the run described in the experimental section, 1.64 moles of ethyl benzoate was produced per mole of starting material. The diazotate formed was not pure. From titrations of the strongly basic solutions produced when it was decomposed in water, one can calculate a neutralization equivalent of 136 g/mole (theory 104 g/mole). Eighty-four percent of the theoretical amount of gas evolved when the crude diazotate was added to 1 N sulfuric acid.

$$K^{+\,-}O\text{-}N{=}NCH_2CH_2CH_2N{=}N\text{-}O^{-}K^{+} \xrightarrow{H_2O,\ H^{+}} 2N_2$$

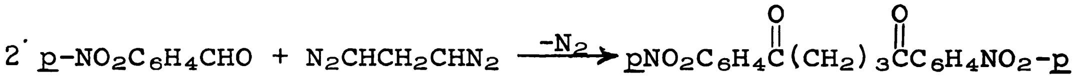
Small amounts of benzoic acid were isolated from the aqueous solutions in which the diazotate had been decomposed indicating that the contaminant was potassium benzoate.

The strongest evidence for the identification of this solid was the fact that 1,3-bisdiazopropane could be prepared from it. When potassium propane-1,3-bisdiazotate was stirred with cyclohexene and methanolic sodium hydroxide, 1,3-bisdiazopropane (yield 49%) was extracted into the cyclohexene phase. This solution was free from contamination by methyl benzoate.

How do we know that the yellow solutions produced when N,N'-trimethylenebis(N-nitrosobenzamide) or potassium propane-1,3-bisdiazotate were stirred with methanolic sodium hydroxide and cyclohexene were actually solutions of 1,3-bisdiazopropane? First, the infrared spectra of these solutions showed a very intense band at 2065 cm^{-1} which is characteristic of the diazo group (15). The solutions evolved a gas and lost their yellow color when stirred with aqueous acid. These facts prove that a diazo compound was present. That the compound actually was 1,3-bisdiazopropane was shown by the preparation of solid derivatives by reaction with benzaldehyde and p-nitrobenzaldehyde.



$$2\ C_6H_5CHO + N_2CHCH_2CHN_2 \xrightarrow{-N_2} C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}C_6H_5$$

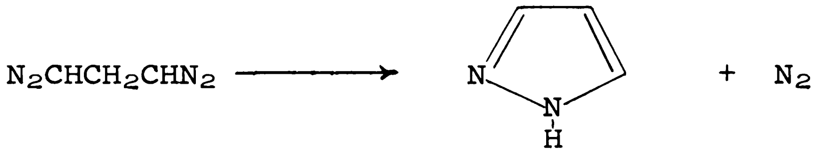


$$2\ \underline{p}\text{-}NO_2C_6H_4CHO + N_2CHCH_2CHN_2 \xrightarrow{-N_2} \underline{p}NO_2C_6H_4\overset{O}{\overset{\|}{C}}(CH_2)_3\overset{O}{\overset{\|}{C}}C_6H_4NO_2\text{-}\underline{p}$$

Benzaldehyde and a solution of 1,3-bisdiazopropane in cyclohexene reacted to form 1,5-diphenyl-1,5-pentanedione in 31% yield. When p-nitrobenzaldehyde was used, 1,5-di(p-nitrophenyl)-1,5-pentanedione was produced in 38% yield. When 1,3-bisdiazopropane was generated from potassium propane-1,3-bisdiazotate in the presence of benzaldehyde, 1,5-diphenyl-1,5-pentanedione was produced in 52% yield.

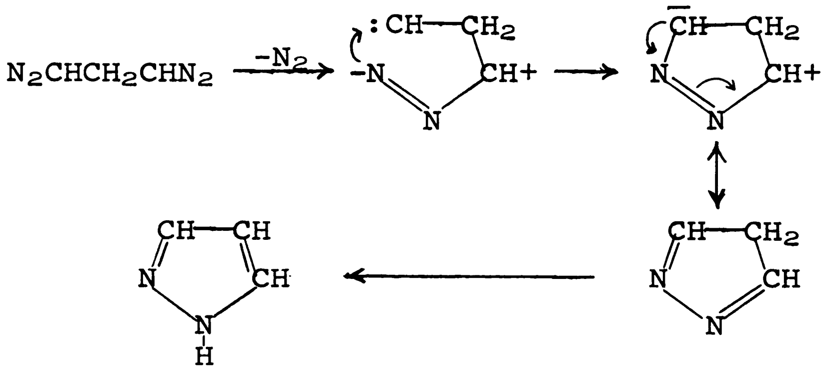
The yields of 1,3-bisdiazopropane were determined by measuring the amount of gas liberated when a sample was decomposed in acid. The calculation assumed that all the gas evolved was derived from 1,3-bisdiazopropane. Whether or not this is true is not known for certain. Applequist and McGreer (19) and Moss (20) have shown that diazoalkanes and solvolysis products are formed simultaneously from reactions that go through a diazotate intermediate. Thus, we might have expected that compounds such as 1-diazo-3-methoxypropane and 3-diazopropene would have been formed during our preparations of 1,3-diazopropane. 3-Diazopropene is red and absorbs visible light much more strongly at 540 mμ than does 1,3-bisdiazopropane. From the low absorbance at 540 mμ of solutions of 1,3-bisdiazopropane, it was calculated that if 3-diazopropene was present, it amounted to less than 4% of all the diazo compound. No products were ever isolated from reactions of these solutions which can be explained as originating from 1-diazo-3-methoxypropane. This indicates that the latter compound was not present in large amounts but certainly does not exclude its presence. Reimlinger (9) was able to obtain bis(3-pyrazoyl)methane in 85% yield from acetylene and 1,3-bisdiazopropane prepared by a method similar to our first method of preparing this compound. His results indicate that at least 85% of the diazo compound present in his solutions was 1,3-bisdiazopropane. If 1,3-bisdiazopropane was not the only diazo compound produced by our methods, it certainly represented a major portion of the diazo compound formed.

2. Cyclization to Pyrazole. 1,3-Bisdiazopropane slowly decomposed at 25° in the dark. A gas bubbled from clear, yellow solutions of this compound in cyclohexene and the yellow color slowly faded. The major decomposition product, pyrazole, was produced in 63% yield.



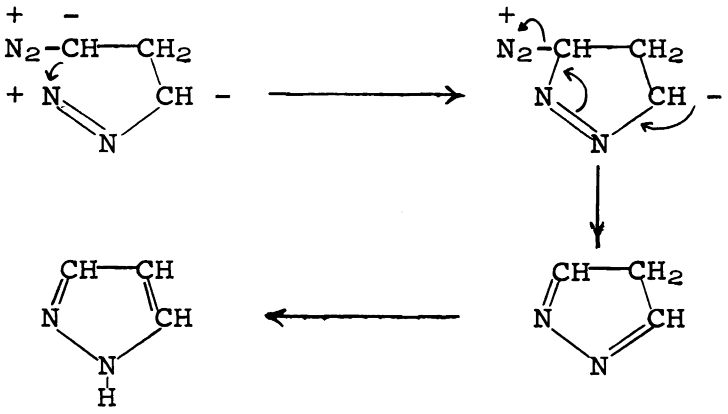
In addition to pyrazole, a small amount of polymeric material was formed.

Two reasonable mechanisms for the formation of pyrazole from 1,3-bisdiazopropane are shown below.



11

Mechanism A

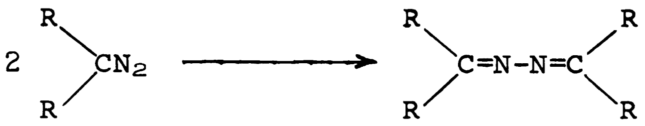


11

Mechanism B

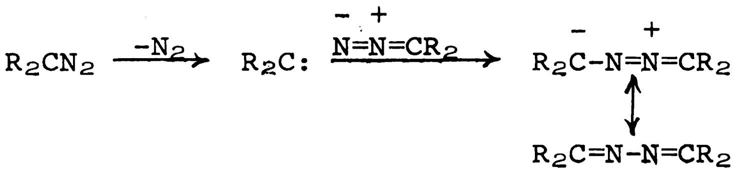
Both schemes involve the formation of an intermediate (11) which isomerizes to pyrazole by the shift of a hydrogen from carbon to nitrogen. Pyrazole is an aromatic species while 11 is not. The gain in stabilization in going from 11 to the lower-energy species, pyrazole, is a powerful driving force for this isomerization.

The intermediate 11 is a cyclic azine. Thermal decomposition of diazoalkanes nearly always gives traces of azines (25).



The amount varies. It is often large for aryldiazomethanes but is usually very small for alkyldiazomethanes. For example, Parham and Hasek have reported that when a solution of diphenyldiazomethane in benzene was refluxed for five days, the azine of benzophenone was produced in 79% yield (26). However, the thermal decomposition of diazocyclohexane gave no azine; cyclohexene was the sole product (25).

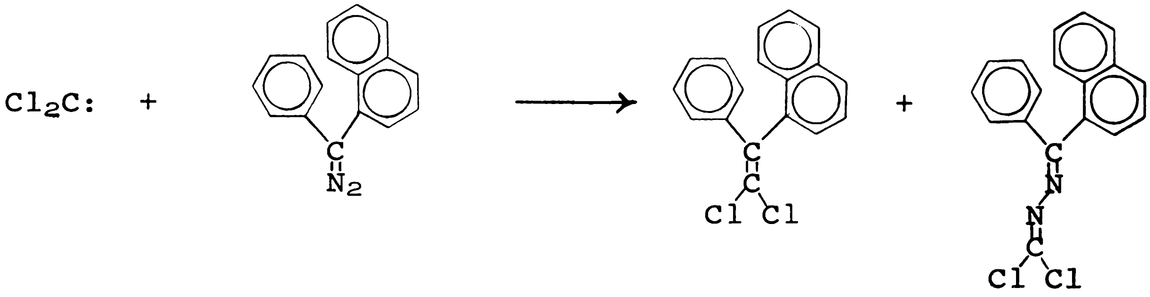
Two mechanisms that are similar to mechanisms A and B have been proposed for the formation of azines from diazoalkanes. The first involves decomposition of a molecule of diazoalkane into a carbene and a molecule of nitrogen. The carbene attacks the terminal nitrogen of a second diazoalkane molecule forming the azine.



$$R_2CN_2 \xrightarrow{-N_2} R_2C: \xrightarrow{\overset{-}{N}=\overset{+}{N}=CR_2} R_2\overset{-}{C}-N=\overset{+}{N}=CR_2 \;\updownarrow\; R_2C=N-N=CR_2$$

This mechanism is an intermolecular version of mechanism A.

Diazoalkanes are known to be sources of carbenes (27). Carbenes are electron deficient species and are expected to attack the positions of high electron density in a diazoalkane molecule. The two limiting resonance structures of the diazo group have negative charges on the terminal nitrogen and diazo carbon. A carbene would be expected to attack at either of these positions. Reimlinger (28) has demonstrated that dichlorocarbene does attack at both positions.

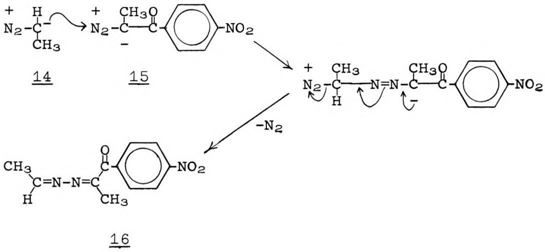


12 52%   13 7%

He reported that α-naphthylphenyldiazomethane and dichlorocarbene reacted to form an olefin (12) by attack at the diazo carbon and an azine (13) by attack at the terminal nitrogen. As the size of the groups attached to the diazo carbon increased a greater proportion of reaction occurred at the more accessible terminal nitrogen and the amount of azine in the product mixture increased. Presumably, a carbene with greater bulk would show a greater preference for attack at the terminal nitrogen. Reimlinger demonstrated that the reaction was a carbene reaction and not attack of trichloromethyl carbanion on the diazo compound. Also, he demonstrated that the azine was stable under the reaction conditions.

Reimlinger (29) measured the rate at which nitrogen was evolved when a solution of diphenyldiazomethane was heated. He found that the rate of decomposition was first order with respect to diphenyldiazomethane. The rate at which diphenyldiazomethane disappeared when solutions of this compound in acetonitrile-water were heated did not change when the concentration of water was varied from 0 to 10 M even though the product composition changed from 0 to 90% diphenylcarbinol (30). All of these observations are consistent with a process in which the diazo compound decomposes unimolecularly to a carbene and nitrogen in the rate determining step. The carbene reacts rapidly with a nucleophile in the product determining step. There is little doubt that aryldiazomethanes such as diphenyldiazomethane do decompose via a carbene mechanism.

However, there is powerful evidence to support the belief that other diazoalkanes react to form azines by other paths. For example, Yates, Farnum and Wiley reported that diazoethane (14) and α-diazo-**p**-nitropropiophenone (15) reacted to form the azine 16 under conditions where each was stable in the absence of the other (31). This observation precludes a unimolecular decomposition of either diazo compound into a carbene and suggests the bimolecular mechanism shown below (31).



Diazoethane behaves as a nucleophile and attacks the more electrophilic diazoketone at the terminal nitrogen. A fact which supports this mechanism is that α-diazopropiophenone, a weaker electrophile than its p-nitro substituted counterpart, reacted with diazoethane more slowly than did α-diazo-p-nitropropiophenone. Also diazomethane, a weaker nucleophile than diazoethane, did not react with either diazoketone. Diazoalkanes undergo numerous reactions where the diazo carbon behaves as a nucleophilic center. Also other reactions are known in which nucleophiles attack the terminal nitrogen of a diazo group (4). This mechanism is an intermolecular version of mechanism B.

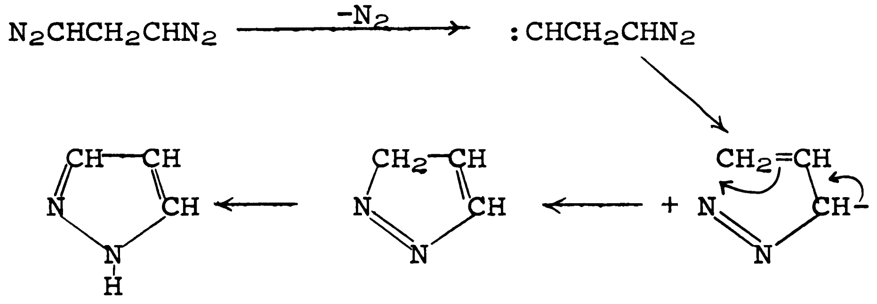
Apparently, diazoalkanes can react to form azines by either of two mechanisms, one which involves a carbene and another which involves a nucleophilic attack of one molecule on the terminal nitrogen of a second molecule. Which one of the mechanism operates appears to depend on the nature of the groups attached to the diazo function.

Do we have any basis for choosing between mechanisms A and B as the actual path by which pyrazole is formed from 1,3-bisdiazopropane? The bimolecular mechanism for azine formation is most likely to occur in reactions where one diazo component is nucleophilic and the other strongly electrophilic. Diazoethane reacts with α-diazo-p-nitropropiophenone, more slowly with α-diazopropiophenone, and not at all with a second molecule of diazoethane (31). The two diazo functions of

1,3-bisdiazopropane are electronically most like the diazo group in diazoethane. Thus, one might be tempted to guess that 1,3-bisdiazopropane would not react by the bimolecular mechanism. However, this reasoning fails to take into account that both reaction sites are in the same molecule. The close proximity of one diazo group to the other should greatly enhance the propensity toward bimolecular reaction. Mechanism B cannot be eliminated.

There is no experimental evidence which favors either mechanism A or B. Both mechanisms have precedent in the literature and must be considered as candidates for the actual reaction path.

A third mechanism can be written for the cyclization of 1,3-bisdiazopropane.

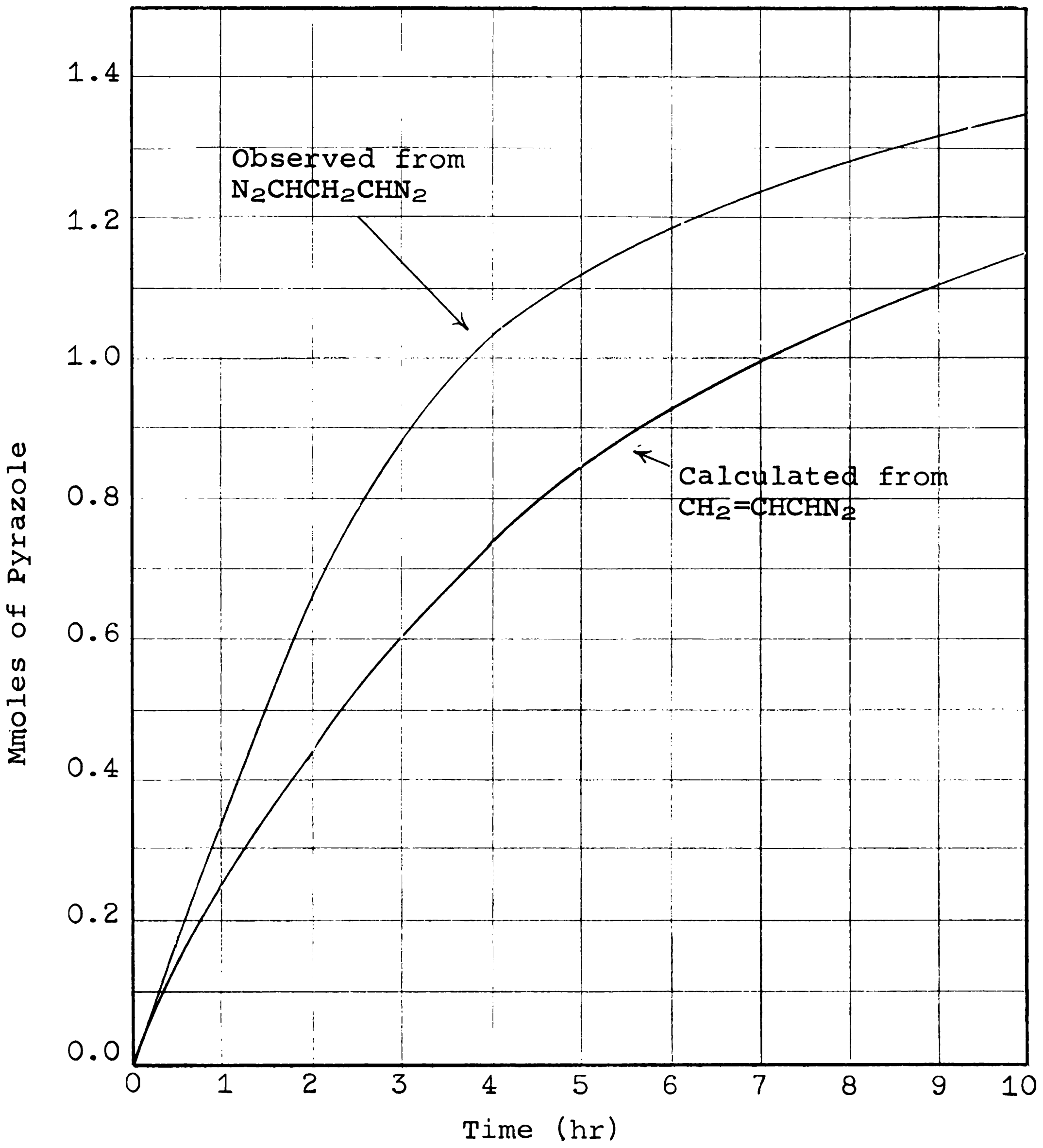


Mechanism C

In this mechanism 1,3-bisdiazopropane loses a molecule of nitrogen to form a carbene. The carbene attacks a C-H bond on the β-carbon and the resulting olefin, 3-diazopropene, cyclizes by an intramolecular 1,3-dipolar addition forming a compound which rapidly isomerizes to pyrazole. Carbenes are easily formed from diazoalkanes (27). One of the most common reactions of an alkyl carbene is insertion into a β-carbon-hydrogen bond to form an olefin (27). The cyclization of 3-diazopropene to pyrazole is a known reaction (11,12). Thus, there is ample precedent for each step of this mechanism; however, two pieces of experimental evidence eliminate mechanism C from consideration.

We prepared 3-diazopropene and found that it slowly disappeared from cyclohexene solution to yield pyrazole in 100% yield. The rate at which it disappeared followed the first order rate law with a rate constant of 6.03×10^{-5} $\sec^{-1}$. Under the same conditions 1,3-bisdiazopropane decomposed to give pyrazole in 49% yield. However, its decomposition was not a clean reaction and as a result, the rate of its disappearance did not fit a simple rate equation. If mechanism C holds, then pyrazole would have appeared at the maximum possible rate if 1,3-bisdiazopropane instantaneously decomposed producing 3-diazopropene in 49% yield and the latter compound cyclized to pyrazole at its normal rate. Figure 1 shows the rate of formation pyrazole from a solution of 2.69 mmoles of 1,3-bisdiazopropane in 40 ml of cyclohexene at 25.0°. The calculated rate at which pyrazole would have been produced from 1.33 mmoles of 3-diazopropene is also plotted in this figure. Pyrazole was produced faster from 1,3-bisdiazopropane than it could have been from 3-diazopropene. This means that 3-diazopropene could not have been an intermediate and that mechanism C was not the actual reaction path.

Figure 1. Plot of the observed and calculated rates of formation of pyrazole in cyclohexene at 25.0°.



The observed data are shown in Table X.

3-Diazopropene is red and absorbs long wavelength light (Figure 7) more strongly than does 1,3-bisdiazopropane which is yellow (Figure 6). If 1,3-bisdiazopropane decomposed to 3-diazopropene at a rate larger than the rate at which 3-diazopropene cyclizes to form pyrazole, a sizeable concentration 3-diazopropene would have built up in the reaction solution and the diazoalkene could have been detected in the visible spectrum of the solution. It was not detected. The only situation which is compatible with this observation and still assumes that mechanism C holds is that 3-diazopropene was produced at a rate which was slow compared to the rate at which it was consumed. In this way only a small, undetectable amount would have been present in the reaction solution. However, since the rate at which pyrazole is produced is proportional to the concentration of 3-diazopropene, pyrazole would have appeared much more slowly than is shown in Figure 1. The calculation of the rate of pyrazole formation from 3-diazopropene shown there assumed that 1,3-bisdiazopropane decomposed instantaneously producing a high concentration of 3-diazopropene at time zero. Since even this rate is smaller than the observed rate, the argument against the intermediacy of 3-diazopropene is even more convincing.

B. 3-Diazopropenes

1. Cyclization to Pyrazoles. 3-Diazoalkenes are red compounds whose solutions absorb light at the blue end of the visible spectrum. When solutions of 3-diazoalkenes were

allowed to stand in the dark at room temperature, the color slowly faded and pyrazoles appeared as products.

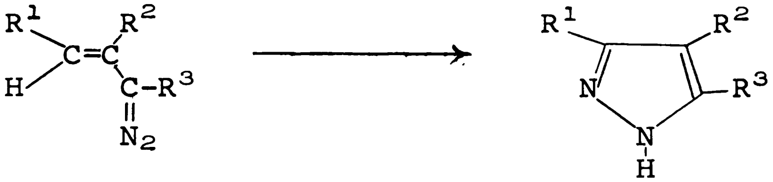


Table I gives the yields of pyrazoles produced from cyclohexene solutions of the corresponding diazoalkenes at room temperature and in the dark.

Table I. Yields[a] of Pyrazoles from 3-Diazoalkenes

R^1	R^2	R^3	Percent Yield Pyrazole
H	H	H	100
H	CH_3	H	100
CH_3	H	H	109
H	H	CH_3	not determined
m-$NO_2C_6H_4$	H	H	89
p-ClC_6H_4	H	H	87
C_6H_5	H	H	86
p-$CH_3C_6H_4$	H	H	not determined

[a] This table summarizes the data presented in experiments C 5 through C 12 of the Experimental Section.

The solutions of 3-diazopropenes used were contaminated with methyl ethyl carbonate and methyl alkenyl ethers. These compounds were also products of the reaction used to prepare the 3-diazopropenes. However, their presence did not interfere

with the cyclization of the diazoalkenes. The rates of disappearance of the 3-diazopropenes fitted the first order rate equation very closely. Thus, the 3-diazopropenes could not have been involved in any significant bimolecular side reactions. The high yields of pyrazoles produced from these 3-diazopropenes also indicated that no major side reactions were occurring. A detailed discussion of the preparations and rates of reaction of the 3-diazopropenes is given later in this thesis.

3-Diazopropenes cyclize spontaneously to pyrazoles. Pyrazoles are formed any time these diazoalkenes are present. Thus, during the preparation of a solution of a 3-diazopropene, a small amount of pyrazole is also formed. In our work the yield of a pyrazole was determined by measuring both the amount of the 3-diazopropene and the amount of the pyrazole present in the solution at a particular instant and then noting the increase in the amount of pyrazole after all the 3-diazopropene had cyclized. 3-Diazo-1-butene cyclized so rapidly that we were not able to measure accurately the amounts of this diazoalkene and of 3(5)-methylpyrazole present in the solution at a given instant. Therefore, the yield of 3(5)-methylpyrazole produced from this diazo compound was not determined. The yield of 3(5)-(p-tolyl)pyrazole was not determined for the same reason.

A source of error in the yield figures given in Table I was our inability to determine accurately the amount of diazo compound in a dilute solution. These measurements were complicated by the fact that the amount of diazo compound was continuously changing. The method used to determine the concentrations of a diazoalkene in cyclohexene solution ultimately depended on measuring the volume of gas evolved when a sample of the solution was added to acid. For concentrated solutions of diazoalkenes, large volumes of gas were liberated and the method was fairly accurate. However, for diazoalkenes which were produced in low yield from their precursors and which were obtained only in dilute solutions, only small amounts of gas were evolved, and the relative errors were large. 3-Diazopropene was easily prepared in fairly concentrated solutions and the reported yield of pyrazole produced from this compound is probably near the true value. However, it was only possible to prepare fairly dilute solutions of 1-diazo-2-butene and trans-3-diazo-1-phenylpropene. The reported yields of pyrazoles produced from these compounds probably are in error by 10% or more. In spite of these uncertainties, the data in Table I do show that the cyclization of 3-diazoalkenes is an efficient reaction and that pyrazoles are produced in quantitative or nearly quantitative yields.

2. Kinetic Results. The rates at which 3-diazoalkenes disappeared from cyclohexene solutions at 25.0° and in the dark were followed by observing the decrease in absorbance of blue light by these solutions. Plots of log $(A-A_{\infty})$ *versus*

time for all these compounds are straight lines showing that their rates of reaction follow the first order rate law. These plots are shown in Figures 2 and 3. The first order rate constants calculated from these data are tabulated in Table II.

Table II. First Order Rate Constants[a] for the Disappearance of 3-Diazoalkenes from Cyclohexene Solutions at 25.0°

3-Diazoalkene	$k \times 10^5$ (sec^{-1})
trans-1-diazo-2-butene	4.51
3-diazo-2-methylpropene	5.15
3-diazopropene	6.03
trans-3-diazo-1-(m-nitrophenyl)propene	19.3
trans-3-diazo-1-(p-chlorophenyl)propene	31.2
trans-3-diazo-1-phenylpropene	36.4
trans-3-diazo-1-(p-tolyl)propene	44.3
3-diazo-1-butene	78.5

[a] This table summarizes the data reported in experiment D 2 of the Experimental Section.

Because only very small amounts of the precursors from which the diazoalkenes were prepared were available, the rates of reaction of all the 3-diazoalkenes except 3-diazopropene were determined only once. The rate of cyclization of 3-diazopropene was measured three times to test the precision of the experimental procedure. The values of the rate constants observed were 6.00, 6.03, and 6.08 x 10^{-5} sec^{-1}. The average deviation from the average rate constant was 0.03 x 10^{-5} sec^{-1}.

Figure 2. Plot of Log of Absorbance *versus* Time for methyl substituted 3-diazopropenes in cyclohexene solutions at 25.0°.

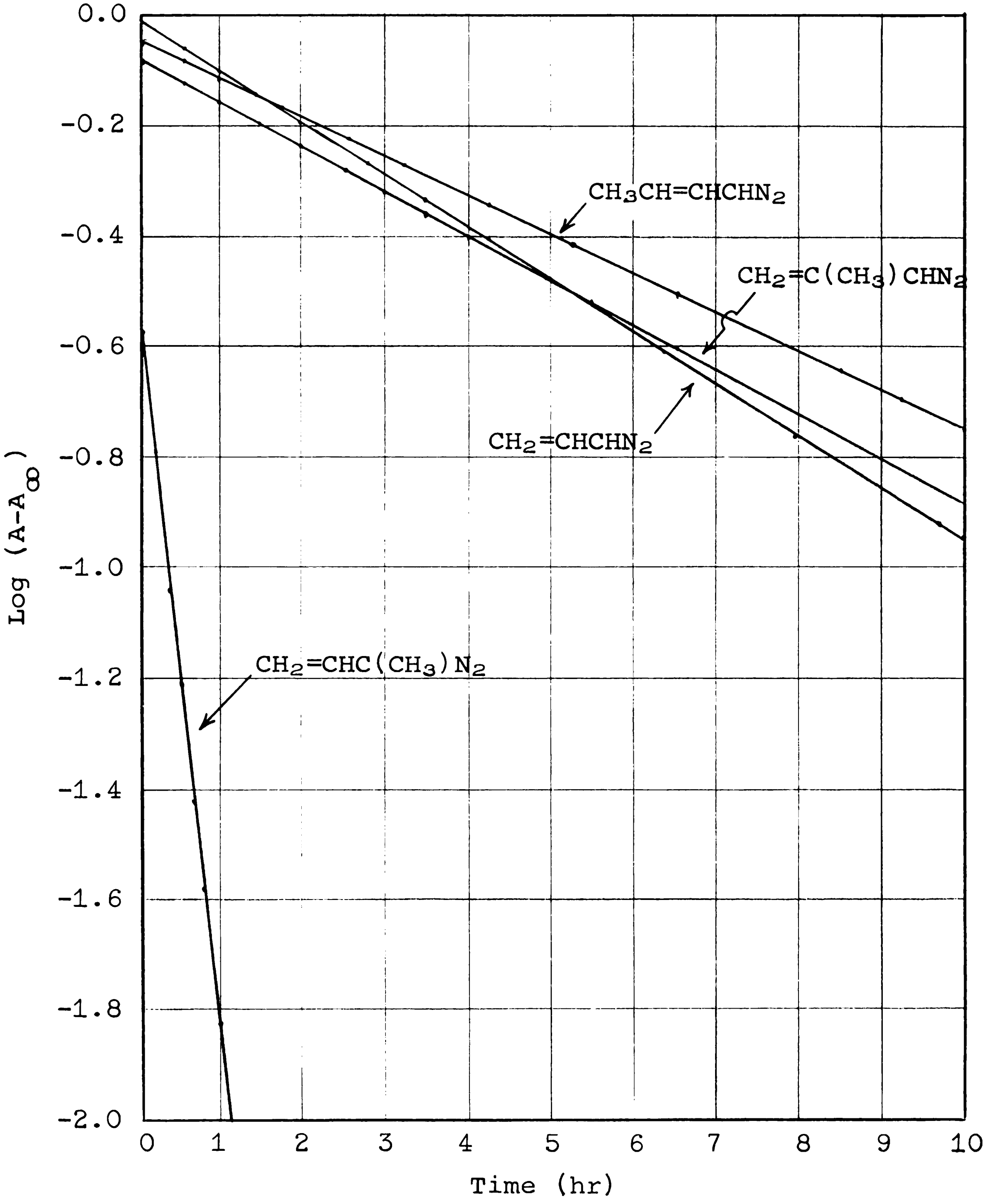
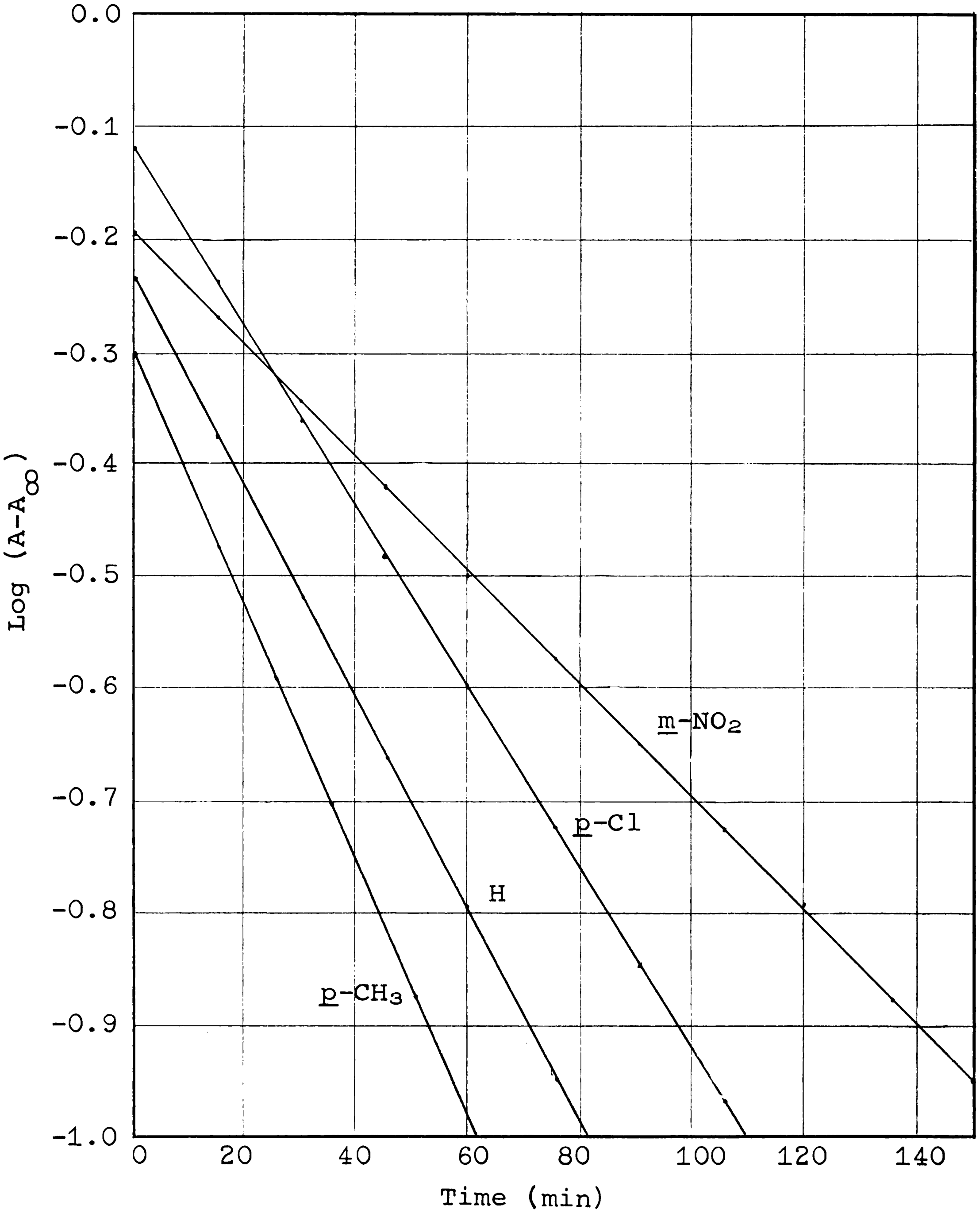


Figure 3. Plot of Log of Absorbance *versus* Time for substituted *trans*-3-diazo-1-phenylpropenes in cyclohexene solutions at 25.0°.

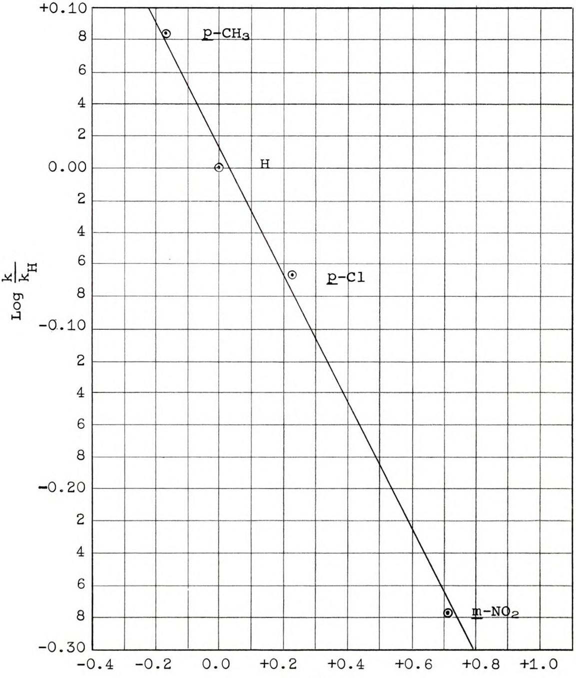


A plot of the log of the relative rate constants of the three substituted trans-3-diazo-1-phenylpropenes with respect to that of the unsubstituted compound (log k/k_H) *versus* the Hammett substituent constants (σ) (32) is a straight line and is shown in Figure 4. The reaction constant (ρ) calculated from these data is -0.40. The correlation coefficient (r), which is a measure of how well the data fit the Hammett equation, is 0.998. This indicates an excellent fit. The calculations of ρ and r were carried out using the method published by Jaffé (32).

Recently Ledwith and Parry have suggested that the cyclization of 3-diazopropene is an intramolecular 1,3-dipolar cycloaddition (13). A comparison of the rate data observed for the cyclization of the eight 3-diazoalkenes mentioned above with data reported for other 1,3-dipolar addition reactions supports this belief.

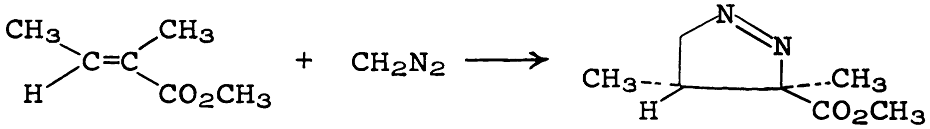
A 1,3-dipolar cycloaddition is a reaction between a multiple bond system, d-e, which is called a dipolarophile, and a 1,3-dipole, a-b-c, which has one mesomeric form in which opposite charges reside on atoms a and c (33). Such reactions form five-membered rings by a concerted mechanism involving a cyclic shift of electrons as symbolized by the arrows in the diagram shown below (34).

Figure 4. Hammett plot[a] for the cyclization of substituted trans-3-diazo-1-phenylpropenes in cyclohexene solutions at 25.0°.

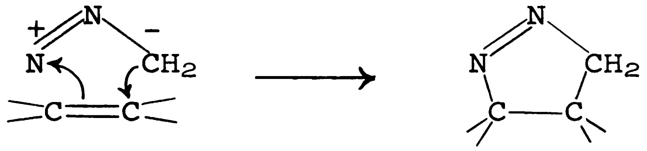


[a] The circles around the points are to help locate the points. They are not indications of the errors in the positions of the points.

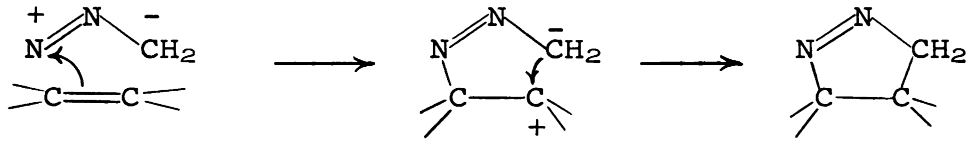
Diazoalkanes are good 1,3-dipoles and their reactions with dipolarophiles are common (33). For example, diazomethane and methyl tiglate react to form the pyrazoline shown below (35).



Two pieces of evidence suggest that 1,3-dipolar cycloadditions are concerted, one-step processes (Mechanism D) and not two-step processes (Mechanism E) (34).



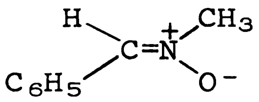
D



E

17

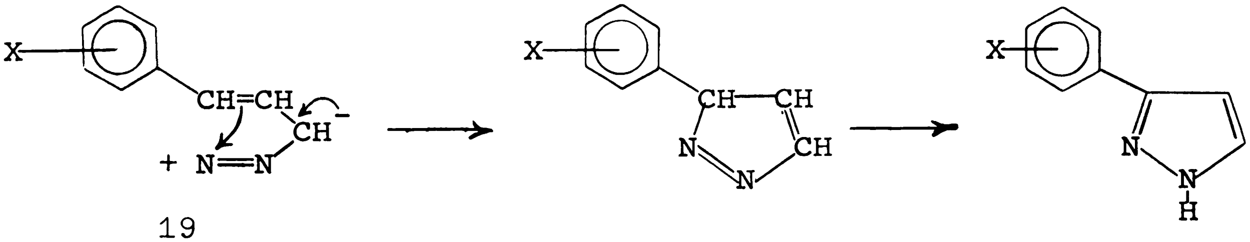
These reactions are stereospecific. cis-Olefins react to give pyrazolines in which the substituents are still cis to one another and trans-olefins react to give products in which the substituents remain trans to one another. The energy required for rotation about a C-C single bond is relatively low. Unless ring closure is extremely fast in intermediate 17, some rotation about the C-C bond would occur and reaction by mechanism E would lead to a mixture of geometric isomers. However, reaction by mechanism D would be stereospecific. Presumably appreciable amounts of charge separation would occur in the transition state leading to 17. If 1,3-dipolar additions proceeded by the two-step mechanism (E), the rates of these reactions should be sensitive to the electronic nature of substituents attached to the dipolarophile. In fact they are not sensitive to changes in the electronic nature of substituents. Huisgen reported that the reaction rate of C-phenyl-N-methylnitrone (18), a 1,3-dipole, with *p*-substituted styrenes only increased by a factor of six as the substituent was varied from methoxy to nitro (34).



18

The ρ value for this reaction was +0.83. These results are best accommodated by the concerted mechanism D.

The rate of cyclization of substituted *trans*-3-diazo-1-phenylpropenes (19) was effected to only a very small extent by altering the nature of the substituent X.



19

When X = *p*-CH_3 the reaction was only 2.3 times faster than when X = *m*-NO_2. The ρ value for the cyclization was -0.40. The small size of ρ indicates that there was very little difference in the charge distribution between the ground state and the transition state for the reaction and suggests that the reaction occurred by a concerted, cyclic shift of electrons.

The slight ability of electron-donating groups to accelerate the rate of cyclization can be rationalized as follows. The nmr resonance signals of the hydrogens on the terminal methylene group in 3-diazopropene appear at τ 8.93 (36). These signals are at unusually high field for vinylic hydrogens. This indicates that there is a partial negative charge on the terminal carbon and that the canonical form <u>20</u> is an important contributor to the structure of 3-diazopropene.

$$\overset{-}{C}H_2\text{-}CH{=}CH\text{-}\overset{+}{N}_2 \longleftrightarrow CH_2{=}CH\text{-}\overset{-}{C}H\text{-}\overset{+}{N}_2$$

<u>20</u>

Cyclization occurs by attack of the diazo group, which carries a partial positive charge, on the terminal carbon. In the transition state for this reaction the amount of negative charge on the terminal carbon is reduced. Electron-donating groups on the phenyl ring of <u>trans</u>-3-diazo-1-phenylpropene will stabilize the transition state relative to the ground state and accelerate the reaction. The actual change in charge density at the 1-carbon must be very small since ρ is small.

Conjugation exerts a greater effect on the relative dipolarophilic activities of olefins than does the electron-donating or withdrawing nature of substituents. For example, diphenyldiazomethane and styrene react at least twenty times more rapidly than the diazo compound and an alkyl-substituted olefin react. This enhancement has been ascribed to the increased mobility of bonding electrons (polarizability) in conjugated systems which results in a greater tendency to enter into cyclic electron shifts (34). The greater reactivity of conjugated systems in comparison to non-conjugated systems is apparent in the rates of cyclization of 3-diazoalkenes. trans-3-Diazo-1-phenylpropene cyclized faster than 3-diazopropene. Substitution of a phenyl ring for a hydrogen in 3-diazopropene increased the rate of reaction by a factor of six.

The most dramatic effect of structure on the rate of cyclization appeared in the series of methyl-substituted 3-diazopropenes.

Table III. The Relative Rates of Cyclization of Methyl-Substituted 3-Diazopropenes in Cyclohexene Solution at 25.0°

Diazoalkene	Relative Rate
$CH_2=CHC(Me)N_2$	13.0
$CH_2=CHCHN_2$	1.00
$CH_2=C(Me)CHN_2$	0.85
$MeCH=CHCHN_2$	0.75

Here, the three structures in which the diazo group is attached to a primary carbon had very nearly the same rate of reaction. 3-Diazo-1-butene, the only compound studied in which the diazo group was attached to a secondary carbon, cyclized thirteen times faster than 3-diazopropene. The greater reactivity of this secondary diazoalkene may be due to the higher ground state energy of secondary diazoalkanes in comparison to primary diazoalkanes. Secondary diazoalkanes are known to be less stable than primary diazoalkanes (4,6).

3. Preparation of 3-Diazopropenes. The 3-diazopropenes were prepared from the corresponding ethyl nitrosocarbamates. The reaction sequence used to prepare these nitrosocarbamates is shown below.

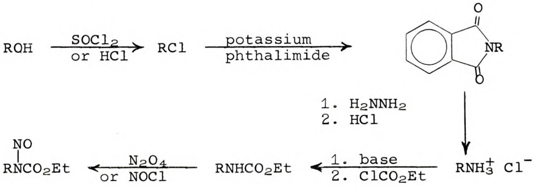
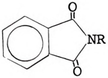


Table IV lists the yields of products for these reactions.

Two reagents were used to nitrosate the ethyl carbamates. Dinitrogen tetroxide and all the ethyl carbamates not containing an aromatic ring reacted cleanly to form their N-nitroso analogs in nearly quantitative yields. However, the phenyl-substituted alkenylcarbamates were only partially converted

Table IV. Yields of Precursors of 3-Diazopropenes

R	Percent Yields[a]				
	RCl		$RNH_3^+Cl^-$	$RNHCO_2Et$	$R\overset{NO}{N}CO_2Et$
CH_2=$CHCH_2$-	-	-	b	91	91
CH_2=$C(CH_3)CH_2$-	b	72	c	67[d]	92
CH_3CH=$CHCH_2$-	44	89	c	46[d]	95
CH_2=$CHCH(CH_3)$-	22	80	c	60[d]	92
m-NO_2-C_6H_4CH=$CHCH_2$-	52	100	96	52	97
p-Cl=C_6H_4CH=$CHCH_2$-	73	81	70	52	97
C_6H_5CH=$CHCH_2$-	53	84	88	85	94
p-CH_3-C_6H_4CH=$CHCH_2$-	70	98	79	85	43

[a] Yields are based on the preceding compound in the reaction sequence unless otherwise specified.

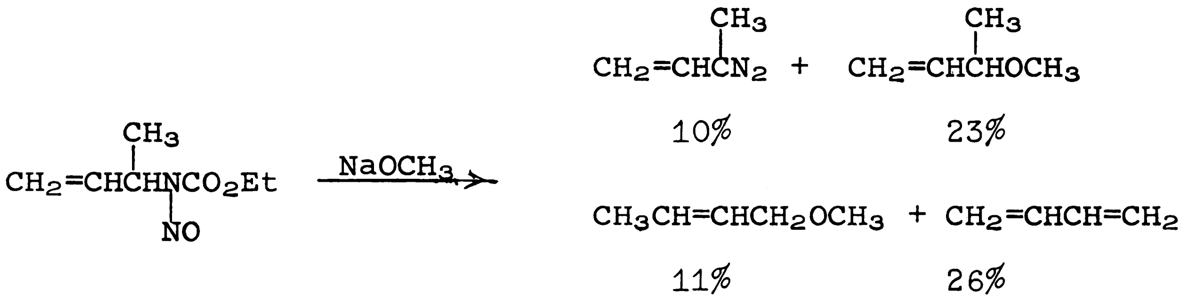
[b] Starting material.

[c] Not isolated.

[d] Yield based on the phthalimide.

to the corresponding alkenylnitrosocarbamates even though all the dinitrogen tetroxide was consumed. The infrared spectrum of the crude product obtained when one equivalent of dinitrogen tetroxide was added to one equivalent of ethyl *trans*-3-phenyl-2-propenylcarbamate showed a strong carbonyl band at 1720 cm^{-1} and a N-H stretching band at 3497 cm^{-1} indicating that there was unreacted starting material present. Evidently a portion of the dinitrogen tetroxide was consumed in side reactions, possibly by electrophilic attack on the aromatic ring or on the olefinic double bond. The unsubstituted, the *p*-chloro-substituted, and the *m*-nitro-substituted ethyl *trans*-3-phenyl-2- propenylnitrosocarbamates could be prepared in quantitative yields by using the milder nitrosating agent, nitrosyl chloride in pyridine (37). This reagent and ethyl *trans*-3-(*p*-tolyl)-2-propenylcarbamate reacted and the related ethyl N-nitrosocarbamate was isolated in 43% yield.

Solutions of 3-diazopropenes were prepared by stirring solutions of the appropriate ethyl alkenylnitrosocarbamate in cyclohexene or di-*n*-butyl ether with methanolic sodium methoxide. The products of these reactions were 3-diazopropenes and compounds which can be rationalized as arising from the carbonium ions produced by loss of nitrogen from the corresponding diazonium ions. For example, when ethyl 1-methyl-2-propenylnitrosocarbamate was treated with sodium methoxide, 3-diazo-1-butene, 3-methoxy-1-butene, *trans*-1-methoxy-2-butene and butadiene were produced.



$$\mathrm{CH_2{=}CH\overset{CH_3}{C}H\underset{NO}{N}CO_2Et} \xrightarrow{\mathrm{NaOCH_3}} \underset{10\%}{\mathrm{CH_2{=}CH\overset{CH_3}{C}N_2}} + \underset{23\%}{\mathrm{CH_2{=}CH\overset{CH_3}{C}HOCH_3}}$$

$$\underset{11\%}{\mathrm{CH_3CH{=}CHCH_2OCH_3}} + \underset{26\%}{\mathrm{CH_2{=}CHCH{=}CH_2}}$$

Methyl ethyl carbonate and nitrogen were probably also formed but no attempt was made to isolate these materials. The yields of all ethers were determined by quantitative glc analysis using an internal standard. The diazoalkenes were allowed to cyclize to pyrazoles and the yields of pyrazoles determined by extracting these weak bases from the reaction solutions with aqueous acid, making the aqueous solutions basic and analyzing the aqueous solutions quantitatively by glc or ultraviolet spectroscopy. Again internal standards were used for the glc analyses. Earlier we saw that 3-diazopropenes cyclize quantitatively to pyrazoles. Thus, the yields of pyrazoles are a good measure of the yields of 3-diazopropenes produced in the original reactions. Tables V and VI list the products and yields of each of these preparations. The reactions listed in Table V were run in di-_n_-butyl ether and those in Table VI in cyclohexene.

Diazo compounds are produced from nitrosocarbamates by initial attack of a base on the carbonyl carbon. The diazotate formed (_21_) adds a proton in protic solvents, and the resulting diazotic acid (_22_) reacts further to give products (16,18,19,20,21,38).

Table V. Products from the Reactions of Ethyl Alkenylnitrosocarbamates and Methanolic Sodium Methoxide in di-*n*-Butyl Ether at 25°

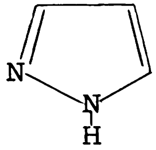
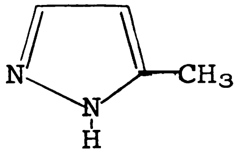
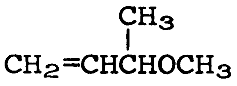
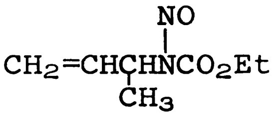
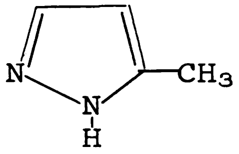
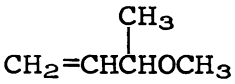
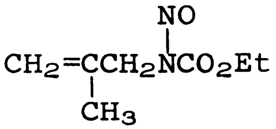
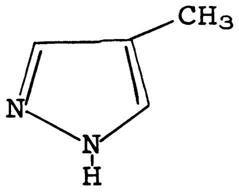
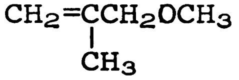
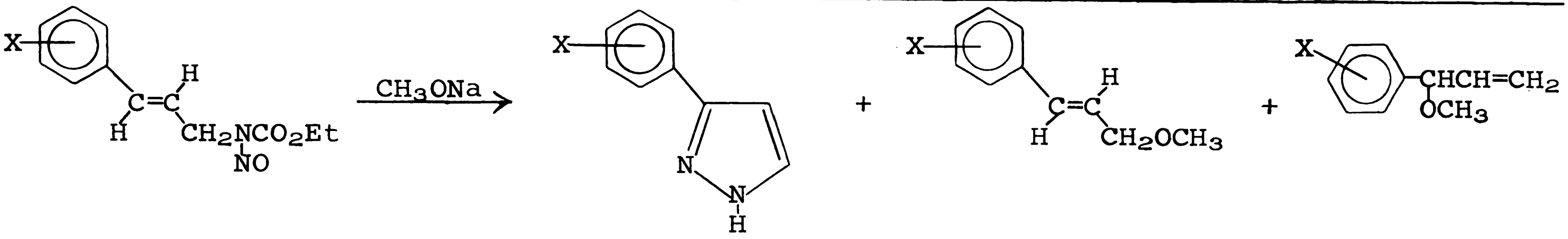
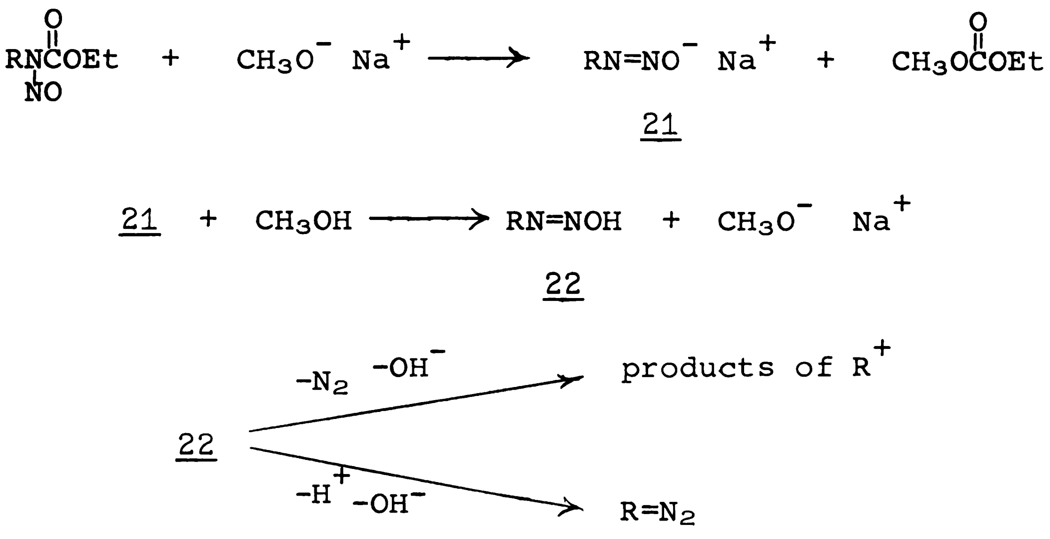
Ethyl Alkenylnitroso-carbamate	Products (Percent Yields from Duplicate Runs)			
 $CH_2{=}CHCH_2\overset{NO}{N}CO_2Et$	 (77,83)	$CH_2{=}CHCH_2OCH_3$ (13,13)		
 $CH_3CH{=}CHCH_2\overset{NO}{N}CO_2Et$	 (33,34)	$CH_3CH{=}CHCH_2OCH_3$ (25,25)	 $CH_2{=}CH\overset{CH_3}{C}HOCH_3$ (7,7)	
 $CH_2{=}CH\underset{CH_3}{C}H\overset{NO}{N}CO_2Et$	 (10,10)	$CH_3CH{=}CHCH_2OCH_3$ (11,11)	 $CH_2{=}CH\overset{CH_3}{C}HOCH_3$ (23,23)	$CH_2{=}CHCH{=}CH_2$ (25,26)
 $CH_2{=}\underset{CH_3}{C}CH_2\overset{NO}{N}CO_2Et$	 (63,67)	 $CH_2{=}\underset{CH_3}{C}CH_2OCH_3$ (12,12)		

Table VI. Products from the Reactions of Ethyl Cinnamylnitrosocarbamates and Methanolic Sodium Methoxide in Cyclohexene at 4°



X	Percent Yield		
m-O_2N	47	41	7
p-Cl[a]	32	22	10
H	22	56	13
p-CH_3	19	36	15

[a] In addition trans-3-(p-chlorophenyl)-2-propen-1-ol was also isolated in 7% yield.



Earlier in this thesis it was shown that the bisdiazotate related to 1,3-bisdiazopropane could be isolated and that when treated with basic methanol, it reacted to form 1,3-bisdiazopropane. There are several other examples cited in the literature describing the preparation and isolation of stable, solid diazotates from reactions of bases with nitrosocarbamates, nitrosoureas and N-nitrosoamides (20,22,23,38). When treated with protic solvents, all these diazotates react to produce diazoalkanes and/or carbonium ion products.

Several pieces of evidence prove that the carbonium ion products do not arise from further reaction of the diazo compound. trans-3-Diazo-1-phenylpropene, trans-3-methoxy-1-phenylpropene, and 3-methoxy-3-phenylpropene were the products formed from ethyl trans-3-phenyl-2-propenylnitrosocarbamate and methanolic sodium methoxide. However, no ethers were formed when trans-3-diazo-1-phenylpropene was stirred with methanolic sodium methoxide under the same conditions as used in its preparation. The diazo compound did not react with basic methanol. Applequist and McGeer (19) showed that diazocyclobutane was stable to the conditions under which it was prepared and that the cyclobutyl ethyl ether and the cyclopropylcarbinyl ethyl ether also observed as products could not have resulted from further reaction of diazocyclobutane. Moss (38) has observed that the 2-octanol produced when potassium 2-octyldiazotate was quenched with heavy water contained almost no carbon-bound deuterium. Therefore, it could not have been formed from 2-diazooctane. These observations indicate that diazoalkanes and carbonium ion products were formed by competitive processes and that the point of separation of the two reaction paths was either the diazotic acid (<u>21</u>) or the diazonium ion. Which one of these compounds was the common precursor to both types of products is not clear.

Table VII summarizes the yields of diazo compounds prepared from eight ethyl alkenylnitrosocarbamates.

The nature of the R group had a strong influence on the partition of the reaction between the paths leading to diazoalkenes and carbonium ion products. One would suspect that those structural features that stabilize diazo compounds would have stabilized the transition states leading to the diazoalkenes and increased the rate at which these compounds were formed. Likewise, those structural features which stabilize carbonium ions should have increased the rate of formation of carbonium ion products. The amounts of the two

Table VII. Yields[a] of Diazoalkenes

R	Percent Yield
CH_2=CHCHN$_2$[b]	80
CH_2=C(CH_3)CHN$_2$[b]	65
CH_3CH=CHCHN$_2$[b]	34
CH_2=CHC(CH_3)N$_2$[b]	10
_m_-NO$_2$-C$_6$H$_4$CH=CHCHN$_2$[c]	47
_p_-Cl-C$_6$H$_4$CH=CHCHN$_2$[c]	32
C$_6$H$_5$CH=CHCHN$_2$[c]	22
_p_-CH$_3$-C$_6$H$_4$CH=CHCHN$_2$[c]	19

[a] Yields are based on ethyl alkenylnitrosocarbamate.

[b] Reaction conditions: Two millimoles of ethyl alkenylnitrosocarbamate in 10 ml of di-_n_-butyl ether was stirred with 6 mmoles of sodium methoxide in 2 ml of methanol at 25° and allowed to stand for 48 hr.

[c] Reaction conditions: Five millimoles of ethyl alkenylnitrosocarbamate in 40 ml of cyclohexene was stirred with 15 mmoles of sodium methoxide in 5 ml of methanol at 4° for 90 min.

types of products formed depend on these rates and as a result on these structural features. Electron-withdrawing substituents stabilize diazo compounds (4,6), and should have increased their yields. Electron-donating substituents stabilize carbonium ions and their presence should have reduced the yields of diazoalkenes by diverting more of the reaction through the path that leads to carbonium ion products. A glance at Table VII bears out this reasoning. In the series of four substituted trans-3-diazo-1-phenylpropenes (last 4 entries), the yield of diazo compound increased in the order of electron-withdrawing power of the substituents, p-CH_3 $<$ H $<$ p-Cl $<$ m-NO_2.

For the four aliphatic 3-diazopropenes, the yield of diazoalkene decreased in the order allyl $>$ 2-methylpropenyl $>$ trans-2-butenyl $>$ 1-methyl-2-propenyl. The relative rates of solvolyses of the corresponding chlorides in 99.5% formic acid, conditions under which all the chlorides react by an S_N1 path, should be a good measure of the relative carbonium stabilities in this series. The relative rates are allyl 1.00, 2-methyl-2-propenyl 0.5, trans-2-butenyl 3550 and 1-methyl-2-propenyl 5670 (39,40). If one excludes the 2-methyl-2-propenyl cation, the order of increasing carbonium stabilities does parallel a decrease in the yields of the corresponding diazoalkenes. The fact that 3-chloro-2-methylpropene solvolyzes via an S_N1 mechanism more slowly than does allyl chloride is somewhat surprising. On the basis of inductive effects, one would have guessed that the presence of a methyl group on the β-carbon would slightly enhance the solvolysis rate. Perhaps steric interference between the methyl group and hydrogens on C-3 in the planar carbonium offsets this acceleration and leads to an overall reduction in the rate of solvolysis.

Up to this point in the discussion of the reactions of diazotates in protic solvents, all the products other than the diazo compounds have been referred to as carbonium ion products. This is a useful but at the same time misleading terminology. A simple-minded picture of the reaction path by which diazotates yield these products and also of the mechanisms of such related reactions as the deaminations of amines and the acid-catalyzed decompositions of diazoalkanes is that they proceed through a carbonium ion which is produced by loss of a molecule of nitrogen from a diazonium ion. In many cases one can qualitatively predict the products of one of these reactions using this picture. Thus, the carbonium ion products derived from ethyl 1-methyl-2-propenylnitrosocarbamate and methanolic sodium methoxide ($CH_2{=}CHCH(OCH_3)CH_3$, $CH_3CH{=}CHCH_2OCH_3$ and $CH_2{=}CHCH{=}CH_2$) are those one would expect from the 1-methyl-2-propenyl cation. However, the situation is much more complicated than this. Often the product ratios and product stereochemistries of such reactions are not the same as those resulting from the same carboniums ions derived from another source (4,41,42,43). Results which will be presented here and results observed by Moss and Lane (38) prove that the solvolyses of diazotates in basic methanol and in water do not proceed exclusively through a free carbonium ion. The diazotates formed by treatment of ethyl 1-methyl-2-propenylnitrosocarbamate and ethyl <u>trans</u>-2-butenylnitrosocarbamate with base should have given the same ratios of solvolysis products if the reaction proceeded through the common, free butenyl carbonium ion. However, they did not. The ratios of <u>trans</u>-1-methoxy-2-butene to 3-methoxy-1-butene produced by these reactions were 0.48 and 3.6 respectively.

Moss and Lane (38) have reported that the hydrolysis of optically active 2-octyl diazotate yielded 2-octanol by two

processes, one of which involved return of the original diazotic acid OH. Reaction by this path gave 2-octanol with predominantly retention of configuration. The remainder of the 2-octanol, which was formed by a second process, contained oxygen present in the solvent and had the inverted configuration. There was little room for a process which yields racemic product. These observations rule out the intervention of a free 2-octyl carbonium ion.

What can be said about the mechanism of the solvolysis of diazotates based on the results reported in this thesis? Two points seem certain. First, the structure of the R group has a strong influence on the partition of the reaction into paths leading to diazoalkane and to solvolysis products. Electron-withdrawing substituents favor the formation of diazoalkanes and electron-donating substituents favor the formation of solvolysis products. Also, solvolysis products are not formed exclusively from free carbonium ions. Different yield ratios for the two possible ethers formed from the 2-butenyl and 1-methyl-2-propenyl systems exclude a major contribution by a reaction path involving the free butenyl carbonium ion.

Table VIII compares the ratios of products obtained from the solvolysis of _trans_-1-chloro-2-butene and 3-chloro-1-butene in acetic acid in the presence of silver acetate (45), from the deamination of _trans_-1-amino-2-butene and 3-amino-1-butene in acetic acid (45), and from reactions of the nitrosocarbamates of these amines in methanolic sodium methoxide and di-_n_-butyl ether.

Table VIII. A Comparison of Product Ratios from the Solvolysis, Deamination and Basic Cleavage of the Chlorides, Amines and Nitrosocarbamates of the trans-2-Butenyl and 1-Methyl-2-Propenyl Systems at 25°

R	Product Ratios $\frac{CH_3CH=CHCH_2-}{CH_2=CHCH(CH_3)-}$		
	$RCl \xrightarrow[Ag^+]{HOAc(45)}$	$RNH_2 \xrightarrow[HOAc]{HNO_2(45)}$	$RN(NO)CO_2Et \xrightarrow[CH_3OH]{NaOCH_3}$
$CH_3CH=CHCH_2-$	1.5	4.0	3.6
$CH_2=CHCH(CH_3)-$	1.3	0.49	0.48

Semenow, Shih, and Young have shown that the ratios of acetates produced by solvolysis of 3-chloro-1-butene and trans-1-chloro-2-butene in acetic acid in the presence of silver acetate are the same within experimental error. This indicates that the free butenyl carbonium ion is a common intermediate in both reactions. However, these authors observed that the acetates with unrearranged structures are the major products produced by deamination of each of the allylic amines. Likewise, we have observed that unrearranged ethers are formed preferentially by solvolysis of the corresponding diazotates. The diazotates were generated in the methanol solutions by attack of base on the ethyl nitrosocarbamates. The large differences in product ratios observed for these last two reactions in comparison to those resulting from solvolysis of the chlorides show that the last two reactions do not proceed through a free carbonium ion. The similarity between the product ratios observed for the deaminations of amines and for basic cleavage of the nitrosocarbamates suggests that the mechanisms of these two reactions are closely related despite the difference in the solvents and acidity of the media.

A great deal of work has been done in an attempt to elucidate the mechanism of amine deaminations (4,41,42,43). These reactions are very complicated and, unfortunately, their mechanisms are not at present fully understood. Zollinger (4) has said, "It must be admitted that the present situation in this field is unsatisfactory in that it is not yet possible to integrate all the observations into one universal mechanism." In view of these uncertainties no attempt will be made here to rationalize the nature and yields of the products formed by treatment of ethyl alkenylnitrosocarbamates with methanolic sodium methoxide in terms of any of the numerous mechanisms proposed for the nitrous acid deaminations of amines.

III. EXPERIMENTAL

A. General

1. Melting Points. Melting points were measured on a Gallencamp melting point apparatus and are uncorrected unless otherwise specified.

2. Microanalysis. Microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

3. Nuclear Magnetic Resonance Spectra. These spectra were recorded on a Varain Model A-60 instrument using tetramethylsilane as an internal standard.

4. Infrared Spectra. Infrared spectra were obtained on a Unicam SP 200 spectrophotometer. The positions of all bands were measured from the nearest polystyrene calibration point (2851, 1603, 1495 and 1029 cm^{-1}).

5. Visible Spectra. The visible spectra of diazo compounds in cyclohexene solutions were recorded on either a Unicam SP 800 or a Beckman DB spectrophotometer. The matched Corex cells had a path length (ℓ) of 0.996 cm. The extinction coefficients (ε) were calculated using the formula:

$$\varepsilon = \frac{A_o - A_\infty}{\ell c}$$

where A_o is the absorbance of the solution at a time t=0 and A_∞ is the absorbance of the same solution several days later ($t=\infty$) after all the diazo compound has cyclized to colorless pyrazole. Since the concentration (c) of the diazo compound in solution is steadily decreasing, it is important to determine the concentration (Procedure A7) at the same time that A_o is measured. Usually the concentration was determined within 3 min of the time when A_0 was measured. Figures 6 through 14 show the visible spectra of 1,3-bisdiazopropane, 3-diazopropene, 3-diazo-2-methylpropene, trans-1-diazo-2-butene, 3-diazo-1-butene, trans-3-diazo-1-(m-nitrophenyl)-propene, trans-3-diazo-1-(p-chlorophenyl)propene, trans-3-diazo-1-phenylpropene and trans-3-diazo-1-(p-tolyl)propene. 3-Diazo-1-butene and trans-3-diazo-1-(p-tolyl)propene cyclized so rapidly that ε values could not be obtained.

6. Ultraviolet Spectra. These spectra were recorded on a Unicam SP 800 spectrophotometer using matched quartz cells with 1.00-cm path lengths.

7. Determination of Yields of Diazo Compounds. Ten milliliters of a solution of diazoalkene in cyclohexene was added via a pressure compensated dropping funnel to a stirred solution of 0.5 g of p-nitrobenzoic acid in 10 ml of diglyme. The determination was carried out in a closed system and the volume of gas liberated was measured over diglyme in a gas measuring burette. The pressure in the system was held at atmospheric pressure by raising or lowering a leveling bulb attached to the gas burette. The number of moles of gas evolved, which is equal to the number of moles of diazoalkene present in the sample, was calculated from the volume of gas liberated using the ideal gas law. The partial pressure (P) of the gas whose volume was being measured is given by

$$P = P_T - P_C f$$

where P_T is the total pressure (equal to atmospheric pressure),

P_c is the vapor pressure of cyclohexene and f is the mole fraction of cyclohexene in the final reaction mixture. The vapor pressure of cyclohexene (bp 83°) was taken to be equal to that of cyclohexane (bp 80.7°) (46). The vapor pressure of diglyme is small at room temperature and was neglected.

8. Gas-Liquid Chromatographic Analysis. All glc analyses were carried out on an Aerograph Model A-350B instrument. An internal standard was used for all quantitative work. The weight of an unknown compound (W_u) in a solution which was being analyzed was calculated using the equation

$$W_u = W_s K \frac{A_u}{A_s}$$

where W_s is the weight of internal standard added to the solution, A_u is the area under the peak due to the unknown compound and A_s is the area under the peak due to the internal standard. K is a relative sensitivity factor which reflects the relative response of the glc detector to equal weights of unknown compound and internal standard. It was determined from a solution containing known weights of the unknown compound (W_u) and internal standard (W_s) using the equation

$$K = \frac{W_u}{W_s} \times \frac{A_s}{A_u}$$

Best results were achieved when the concentrations of components in the standard solution were the same as in the solution being analyzed. The areas under glc peaks were measured using a K and E compensating polar planimeter (Model 620000).

All standard solutions were prepared by carefully weighing out samples of compounds to the nearest 0.0001 g and dissolving them in the desired solvents. Volatile compounds were weighed in small, sealed, glass capsules which were then crushed under the surface of the solvent.

B. Preparation of Precursors to Diazo Compounds

1. N,N'-Trimethylenebisbenzamide. Benzoyl chloride (140 g, 1.00 mole) was added over a period of 55 min to a well-stirred solution of 29.6 g (0.40 mole) of 1,3-diaminopropane and 60 g (1.50 moles) of sodium hydroxide in 600 ml of water. An ice bath held the temperature of the reaction mixture below 10°. After stirring the slurry for an additional 1 hr, it was filtered. The solid, white product was washed with a large amount of water and air dried. The crude amide was dissolved in 300 ml of boiling 1:1 ethanol-benzene and this solution was diluted with 300 ml of benzene. After being cooled, 86.2 g of N,N'-trimethylenebisbenzamide (mp 148.5°, lit. 47, mp 147-148°) precipitated. The mother liquor was concentrated and a second crop of product (9.3 g, mp 146.0-147.5°) was isolated. The yield of product (total 95.5 g) based on 1,3-diaminopropane was 85%.

2. N,N'-Trimethylenebis(N-nitrosobenzamide). A cold solution of dinitrogen tetroxide (48) (100 mmoles) in 50 ml of 1:1 acetic acid-acetic anhydride was slowly added to a stirred solution of 14.1 g. (50 mmoles) of N,N'-trimethylenebisbenzamide in 100 ml of 1:1 acetic acid-acetic anhydride

at 5^{o}. After being stirred at 5^{o} for 20 min, the yellow solution was poured into 600 ml of ice water. A yellow oil separated and quickly crystallized. The product, 16.2 g (yield 95%) of a yellow solid, was washed with water and air dried, mp 78^{o} (dec.), lit. (9) mp 83-84.5^{o} (dec.). The infrared spectrum and ^{1}H nmr spectrum of this material are shown in Figures 15 and 32 respectively.

3. Potassium Propane-1,3-bisdiazotate. A 250-ml round-bottomed three-necked flask was fitted with a condenser, nitrogen inlet, magnetic stirrer and dropping funnel. It was flame dried and flushed with nitrogen. Potassium (0.80 g, 0.020 g atom) was dissolved in 3.68 g (0.080 mole) of absolute ethanol and 20 ml of anhydrous ether in this flask. After the potassium had dissolved, an additional 50 ml of anhydrous ether was added. Slowly a solution of 1.70 g (5.0 mmoles) of N,N'-trimethylenebis(N-nitrosobenzamide) in 60 ml of anhydrous ether was added drop by drop. Immediately a white precipitate formed. The slurry was forced through a fine glass frit filter by 6 psig nitrogen pressure. The white solid was washed twice (under nitrogen) with anhydrous ether and dried at 0.1 mm pressure for 20 min at room temperature (yield 1.28 g).

The product was stable under nitrogen up to 168^{o} where it decomposed explosively. It rapidly decomposed in water, evolving a gas and leaving a basic solution. From titrations of these solutions with standard dilute hydrochloric acid to a phenolphthalein end point, a neutralization equivalent of 136 g of product per mole of base was calculated (theoretical NE 104). Similar preparations gave a product which evolved 84% of the theoretical amount of gas when decomposed in water. The infrared spectrum (Fluorolube mull) showed bands at 2908 (s), 2878(s), 1603(s), 1571(s), 1385(s), cm^{-1} and (Nujol mull) 1603(s), 1571(s), 1162(s), 1085(s), 840(w) and 800(m) cm^{-1}. A composite infrared spectrum is shown in Figure 16.

4. Ethyl Allylcarbamate. Ethyl chloroformate (54.3 g, 0.5 mole) was added dropwise to a well-stirred solution of 57 g (1.0 mole) of allylamine in 150 ml of anhydrous ether cooled in an ice bath. The rate of addition was adjusted so that the temperature stayed below 10°. When the addition was complete, a second portion (54.3 g, 0.5 mole) of ethyl chloroformate was slowly added simultaneously with a solution of 40 g (1.0 mole) of sodium hydroxide in 100 ml of water. After being stirred for 1 hr, the two phases were separated and the aqueous phase was extracted with 100 ml of ether. The combined organic phase was washed with 1 N aqueous hydrochloric acid, water and 5% aqueous sodium bicarbonate solution, then dried over anhydrous magnesium sulfate. The ether was removed by distillation. The product distilled through a 20-cm Vigreaux column as a clear, colorless liquid (102.9 g, yield 91%) which had the following properties: bp_{50} 111-114° (lit. 49, bp_{768} 194.5-195°); infrared spectrum (neat) 3370(s), 2995(m), 1700(s), 1532(s), 1648(m) and 1248(s) cm^{-1}; ^{1}H nmr

spectrum (neat) τ 8.83 (3.0 H, triplet, J=7 cps), τ 6.25 (1.9 H, multiplet), τ 5.92 (2.0 H, quartet, J=7 cps), τ 5.15 to τ 3.67 (3.7 H, multiplet).

5. Ethyl Allylnitrosocarbamate. A cold solution of 11.0 g (120 mmoles) of dinitrogen tetroxide (48) in 60 ml of anhydrous ether was added to a solution of 15.5 g (120 mmoles) of ethyl allylcarbamate in 60 ml of anhydrous ether at -50°. The blue solution was stirred under nitrogen and allowed to warm to 10°. The resulting yellow solution was washed with 5% sodium bicarbonate solution and water. After the solution was dried over anhydrous magnesium sulfate, the ether was removed at 35° under reduced pressure. The product, 17.1 g (yield 91%) of clear, faintly yellow liquid, remained. The infrared and ^{1}H nmr spectra of this compound are shown in Figures 17 and 33.

6. N-(2-Methyl-2-propenyl)phthalimide. 3-Chloro-2-methylpropene (70 g, 0.76 mole) was added to a slurry of 154 g (0.80 moles) of potassium phthalimide in 300 ml of dimethylformamide. The mixture was heated to 120° and stirred at that temperature for 30 min. All the solid dissolved. After being stirred at 155° for an additional 95 min, the solution was cooled and poured into 400 ml of cold water. The tan solid which separated was collected, washed with a large amount of water and air dried. The crude product (128 g) was dissolved in 300 ml of hot ethanol and the solution was cooled in ice; 111 g (yield 72%) of light-tan solid separated,

mp 86-88°. After one more recrystallization from hot ethanol, the product was white and had a mp of 87-88°, lit 49a, mp 88.5-89°.

7. Ethyl 2-Methyl-2-propenylcarbamate. A solution of 109 g (0.55 mole) of N-(2-methyl-2-propenyl)phthalimide and 30 g (0.60 mole) of 99% hydrazine hydrate in 350 ml of 95% ethanol was refluxed for 4 hr. Phthalhydrazide separated. The resulting thick, white slurry was cooled to room temperature and 51 ml (0.60 mole) of concentrated hydrochloric acid was added. The slurry was filtered. The phthalhydrazide was slurried twice with 150-ml portions of water and filtered. The water and ethanol were stripped from the combined filtrates at 60° under reduced pressure. The solid which remained was dissolved in 50 ml of water and the solution was cooled in ice. Ether (100 ml) was added and the solution was made strongly basic by slowly adding 26 g (0.65 mole) of sodium hydroxide dissolved in 50 ml of water. The two phases were separated and the aqueous phase was extracted with three 100-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate. The carbamate of 3-amino-2-methylpropene was prepared directly from this solution as described below.

The ether solution of 3-amino-2-methylpropene was poured into a 1-liter, three-necked, round-bottomed flask which was equipped with two dropping funnels, a thermometer and a paddle stirrer. Slowly one-half of 59 g (0.55 mole) of ethyl chloroformate was added drop by drop at 4°. A solution of 21.8 g

(0.55 mole) of sodium hydroxide in 50 ml of water was slowly added simultaneously with the second half of the ethyl chloroformate. The temperature was held below 10° using an ice bath. The two phases were separated and the organic layer was extracted with 5% aqueous sulfuric acid, 5% sodium bicarbonate solution and water. The solution was dried over anhydrous magnesium sulfate and the ether was removed at reduced pressure. The residue was distilled through a 20-cm Vigreaux column. The product, 52 g of clear, colorless liquid, had the following properties: bp_{22} 104-106°; infrared spectrum (CCl_4) 3490(m), 2990(m), 1721(s), 1657(m), 1515(s), 1218(s) and 905(m) cm^{-1}; ^{1}H nmr spectrum τ 8.83 (3.0 H, triplet, J=7 cps), τ 8.20 (3.0 H, singlet) τ 6.33 (2.0 H, doublet, J=6 cps), τ 5.92 (2.1 H, quartet, J=7 cps), τ 5.19 (1.9 H, multiplet) and τ 3.69 (0.9 H, broad singlet). The yield of ethyl 2-methyl-2-propenylcarbamate based on N-(2-methyl-2-propenyl)phthalimide was 67%.

8. Ethyl 2-Methyl-2-propenylnitrosocarbamate. This compound was prepared in 93% yield from ethyl 2-methyl-2-propenylcarbamate and dinitrogen tetroxide following the procedure described for the preparation of ethyl allylnitrosocarbamate (Procedure B5). The product is a stable, yellow liquid whose infrared and ^{1}H nmr spectra are shown in Figures 18 and 34.

9. 3-Chloro-1-butene and trans-1-Chloro-2-butene. trans-Crotyl alcohol (100 g, 1.39 moles) was slowly poured into 300 ml of concentrated hydrochloric acid. The mixture was stirred at room temperature for 10 hr and the two phases were separated. After being dried over anhydrous magnesium sulfate,

the organic phase was fractionated through a 40-cm column packed with glass helices. 3-Chloro-1-butene (28.0 g, yield 22%) distilled as a clear, colorless liquid, bp 63.0-65.0°, n_D^{25} 1.4131 (lit. 50, bp 63.5-64.0, n_D^{27} 1.4104) and *trans*-1-chloro-2-butene (55.4 g, yield 44%) as a clear, colorless liquid, bp 82.0-83.0°, n_D^{24} 1.4322 (lit. 50, bp 84-85°, n_D^{27} 1.4288). The ^{1}H nmr spectrum (neat) of 3-chloro-1-butene showed a doublet (2.0 H, J=6 cps) at τ 8.47, a quintet (0.9 H, J=6.7 cps) at τ 5.52, a multiplet (2.0 H) between τ 4.61 and τ 5.10 and a multiplet (1.1 H) between τ 3.74 and τ 4.40. The ^{1}H nmr spectrum (neat) of *trans*-1-chloro-2-butene showed a doublet which was further split (3.0 H, $J \cong 5$ cps) at τ 8.34, a doublet which was further split (2.0 H, $J \cong 5$ cps) at τ 6.02 and a multiplet (2.0 H) between τ 3.90 and τ 4.74.

10. N-(*trans*-2-Butenyl)phthalimide. The procedure used was described by J. D. Roberts and R. H. Mazur (51). Ninety-nine grams (yield 89%) of granular, white solid (mp 74-76°, lit. 51, mp 75.2-75.8°) was obtained from 50 g (0.55 mole) of *trans*-1-chloro-2-butene and 126 g (0.58 mole) of potassium phthalimide in 250 ml of dimethylformamide.

11. Ethyl *trans*-2-Butenylcarbamate. This compound was prepared using the same procedure as was used to prepare ethyl 2-methyl-2-propenylcarbamate (Procedure B7). *trans*-1-Amino-2-butene was prepared by refluxing a solution of 97.6 g (0.49 mole) of N-(*trans*-2-butenyl)phthalimide and 21 g (0.53 mole) of 99% hydrazine hydrate in 300 ml of 95% ethanol for

12 hr. A solution of the amine in ether was treated with 52.5 g (0.49 mole) of ethyl chloroformate and 19.4 g (0.49 mole) of sodium hydroxide in 50 ml of water. The product was isolated by distillation through a 20-cm Vigreaux column and had the following properties: clear, colorless liquid, bp_{19} 108-109°, lit. 14, bp_8 94°; infrared spectrum (CCl_4) 3485(m), 2990(m), 1720(s), 1505(s), 1222(s) and 975(m) cm^{-1}; ^1H nmr spectrum τ 8.82 (3.1 H, triplet, J=7 cps), τ 8.35 (2.9 H, doublet with finer splitting, $J \cong 4$ cps), τ 6.32 (2.0 H, multiplet), τ 5.94 (2.0 H, quartet, J=7 cps), τ 4.27 to τ 4.61 (1.9 H, multiplet) and τ 3.79 (1.0 H, broad singlet). The yield (31.9 g) of *trans*-2-butenylcarbamate based on the phthalimide was 46%.

12. *Ethyl trans-2-Butenylnitrosocarbamate*. This compound was prepared using the procedure described for the preparation of ethyl allylnitrosocarbamate (Procedure B5). Dinitrogen tetroxide (11.0 g, 0.12 mole) and ethyl *trans*-2-butenylcarbamate (17.2 g, 0.12 mole) reacted in ether to give 19.6 g (yield 95%) of the desired product. The infrared and ^1H nmr spectra of this stable, yellow liquid are shown in Figures 19 and 35.

13. *N-(1-Methyl-2-propenyl)phthalimide*. The procedure followed is described by J. D. Roberts and R. H. Mazur (51). Forty-five grams (yield 80%) of white, crystalline product (mp 82-84°, lit. 51, mp 85.0-85.6°) was obtained from 25 g (0.28 mole) of 3-chloro-1-butene and 55.5 g (0.30 mole) of potassium phthalimide in 100 ml of dimethylformamide.

14. Ethyl 1-Methyl-2-propenylcarbamate. The procedure used here is the one described for the preparation of ethyl 2-methyl-2-propenylcarbamate (Procedure B7). 3-Amino-1-butene was prepared by refluxing a solution of N-(1-methyl-2-propenyl)phthalimide (43.6 g, 0.22 mole) and 10 g (0.25 mole) of 99% hydrazine hydrate in 190 ml of 95% ethanol for 2 hr. A solution of the amine in ether was treated with 23.9 g (0.22 mole) of ethyl chloroformate and 8.8 g (0.22 mole) of sodium hydroxide in 20 ml of water. The product was isolated by distillation through a 20-cm Vigreaux column and had the following properties: clear, colorless liquid; bp_{18} 86-88°, lit. 14, bp_8 80°; infrared spectrum (CCl_4) 3485(m), 2990(m), 1721(s), 1645(w), 1503(s), 1220(s) and 930(m) cm^{-1}; ^1H nmr spectrum τ 8.82 and τ 8.78 (6.0 H, overlapping triplet and doublet each with J=7 cps), τ 5.94 (quartet with J=7 cps and an overlapping multiplet, 2.9 H), τ 4.69 to τ 5.17 (1.9 H, multiplet) and a multiplet between τ 3.82 and τ 4.45 which is superimposed on a broad singlet at τ 3.75 (total 2.1 H). The yield (18.8 g) of ethyl 1-methyl-2-propenylcarbamate based on N-(1-methyl-2-propenyl)phthalimide was 60%.

15. Ethyl 1-Methyl-2-propenylnitrosocarbamate. This compound was prepared using the procedure described for the preparation of ethyl allylnitrosocarbamate (Procedure B5). Dinitrogen tetroxide (5.5 g, 60 mmoles) and 8.6 g (60 mmoles) of ethyl 1-methyl-2-propenylcarbamate were combined and 9.5 g (yield 92%) of yellow, liquid product was isolated. The

infrared and ^{1}H nmr spectra of this compound are shown in Figures 20 and 36.

16. *trans*-3-(*m*-Nitrophenyl)-2-propenal. A solution of 15.1 g (0.10 mole) of *m*-nitrobenzaldehyde in 40 ml (31 g, 0.74 mole) of acetaldehyde was stirred vigorously while being cooled in an ice bath. Two milliliters of 25% methanolic potassium hydroxide solution was added. After 3.0 min, 40 ml of acetic anhydride was added and the clear, amber solution was allowed to warm to room temperature. One hundred milliliters of 1 N aqueous sulfuric acid was added and the solution was refluxed for 30 min. When the solution was cooled in ice, 12.6 g of off-white solid separated, mp 104-108°. This product was dissolved in 50 ml of hot acetic acid and the solution was diluted with 30 ml of hot water. Purified product (9.6 g, yield 56%, mp 109-110.5°) separated when the solution was cooled. A second recrystallization from 2:1 benzene-hexane gave white crystals with mp 110.5-111.5° (lit. 52, mp 114-115°): infrared spectrum ($HCCl_3$) 2940(w), 2851(w), 1680(s), 1630(m), 1538(m), 1355(s), 1120(s) and 975(m) cm^{-1}; ^{1}H nmr spectrum ($DCCl_3$) τ 3.20 (0.9 H, a doublet, J=16.5 cps, with both lines further split into doublets, J=7.5 cps), τ 2.56 to τ 1.50 (5.0 H, multiplet) and τ 0.20 (1.0 H, doublet, J=7.5 cps).

17. *trans*-3-(*m*-Nitrophenyl)-2-propen-1-ol. Sodium borohydride (7.6 g, 0.20 mole) was slowly added to a slurry of 90.6 g (0.51 mole) of *trans*-3-(*m*-nitrophenyl)-2-propenal

in 500 ml of isopropanol. The temperature rose to 41° and all the solid dissolved. Soon, however, a thick brown solid precipitated. After 10 hr, 200 ml of 10% aqueous sodium hydroxide solution was added and the mixture was refluxed for 1 hr. All solids dissolved. When cooled, the solution separated into two layers. The isopropanol was stripped from the organic layer and the residual oil was taken up in ether. This solution was washed with 2% aqueous sulfuric acid, 5% aqueous sodium bicarbonate solution and water. The solution was dried over anhydrous magnesium sulfate, the ether was removed and the residue was distilled through 20-cm Vigreaux column. The product distilled as a clear, colorless liquid ($bp_{0.8}$ 151-157°, yield 58%), which solidified on cooling, mp 42-48°. The solid was recrystallized from 2:3 ethyl acetate-hexane giving fine, white needles, mp 51.0-51.5° (lit. 53, mp 51-51.5°). The infrared spectrum (CCl_4) showed bands at 3650(w), 2940(w), 2875(w), 1540 (m), 1350(s), 1090(m) and 975(m) cm^{-1}; ^{1}H nmr spectrum τ 6.37 (1.0 H, broad singlet), τ 5.61 (1.8 H, doublet, J=3.5 cps), τ 3.45 (1.9 H, multiplet) and τ 2.79 to τ 1.83 (4.0 H, multiplet).

18. _trans_-3-Chloro-1-(_m_-nitrophenyl)propene. Ten grams (56 mmoles) of _trans_-3-(_m_-nitrophenyl)-2-propen-1-ol in 20 ml of chloroform was treated with a solution of 8.3 g (70 mmoles) of thionyl chloride and 6.0 g (76 mmoles) of pyridine in 10 ml of chloroform at 4°. The addition required 35 min. The solution was refluxed for 1 hr, cooled, extracted with cold

The German looked at the girl in amazement. "You dare call me a bastard? Take off her clothes. The soldiers pulled her up, and ripped the nightgown off her, expozing her pale body to the light. Her small Breasts quivered as the girls shivered with cold. Her light pubic hair glistened in the light. The Captain took off his pants, his huge pulsating organ standing hard away from his body. He said, See this bitch? suck it off. Eat me up till I come in your mouth. You French broads suck like vacuum cleaner;

Pussy power

water and dried over magnesium sulfate. The chloroform was stripped off and the tan solid (10.4 g) which remained was heated to boiling with 100 ml of hexane. The hot solution was decanted from an insoluble residue. The residue was again heated to boiling with 20 ml of hexane and the liquid decanted into the first hexane solution. After the solution was cooled in ice, 5.7 g (yield 52%) of light yellow needles (mp 77-80°) separated. After a second recrystallization from 100 ml of hot hexane, the product had the following properties: faintly yellow needles; mp 81-82° (lit. 54, mp 78°); infrared spectrum (CCl_4) 3090(w), 3040(w), 2950(w), 2855(w), 1535(s), 1350(s), 970(s) and 670(s) cm^{-1}; ^1H nmr spectrum ($DCCl_3$) τ 5.74 (1.8 H, doublet, J=5.7 cps), τ 3.89 to τ 3.12 (2.1 H, an AB quartet, J=16 cps, with the high field doublet further split into two triplets, J=5.7 cps) and τ 2.74 to τ 1.79 (4.0 H, multiplet).

19. <u>N-[trans-3-(m-Nitrophenyl)-2-propenyl]phthalimide</u>. A slurry of 31.5 g (0.17 mole) of potassium phthalimide and 30 g (0.15 mole) of <u>trans</u>-3-chloro-1-(<u>m</u>-nitrophenyl)propene in 250 ml of dimethylformamide was stirred at 25° for 1 hr and at 40° for 6 hr. The slurry was poured into 1 liter of cold water and filtered. The tan solid which separated was washed with 300 ml of water and air-dried, mp 149-151°. The yield of product was 57.4 g. A hot solution of 2.0 g of the product in acetone was treated with Norit and filtered. Light yellow crystals (0.97 g, mp 153.3-153.8°) precipitated

when the solution was cooled. The infrared spectrum (CCl_4) of the product showed adsorption bands at 2930(w), 1715(s), 1538(m), 1390(s), 1350(s), 970(m) and 960(m) cm^{-1}.

20. Hydrochloride of trans-3-Amino-1-(m-nitrophenyl)-propene. Thirty-one grams of the desired amine hydrochloride was obtained by refluxing a solution of 0.15 mole of N-[trans-3-(m-nitrophenyl)-2-propenyl]phthalimide and 15 g (0.30 mole) of 99% hydrazine hydrate in 500 ml of methanol for 4.5 hr. The procedure followed in this preparation was the same as that used for the preparation of the hydrochloride of trans-3-amino-1-phenylpropene (Procedure B33). Most of the brown color was washed out of the crude product with cold acetone. The final product was a cream-colored solid (mp 180-182° with dec.) whose infrared spectrum (KBr pellet) showed intense absorption between 3400 and 2500 cm^{-1} and bands at 1535(s), 1500(m), 1350(s), 1100(m), 970(m), 810(m) and 730(m) cm^{-1}. The yield of amine hydrochloride based on starting phthalimide was 96%.

21. Ethyl trans-3-(m-Nitrophenyl)-2-propenylcarbamate. This compound was prepared using the procedure described for the preparation of ethyl trans-3-phenyl-2-propenylcarbamate (Procedure B34). Nineteen and one-half grams (yield 52%) of product was obtained from 34.8 g (about 0.15 mole) of crude hydrochloride of trans-3-amino-1-(m-nitrophenyl)propene. The product crystallized from ether as long white needles (mp 92.0-92.5°) and had the following properties: infrared spectrum (CCl_4) 3490(w), 3000(w), 2950(w), 1720(s), 1535(s), 1510(s), 1222(m) and 970(m) cm^{-1}; ^1H nmr spectrum (acetone)

τ 8.78 (3.3 H, triplet, J=6.8 cps), τ 5.89 (quartet, J=6.8 cps, overlapping with a doublet, J=6 cps, centered at τ 6.02 in which both lines were further split into doublets, J=4.2 cps, total 4.0 H), τ 3.90 to τ 3.13 (3.0 H, an AB quartet, J=16.0 cps, in which the high field doublet was further split into two triplets, J=4.2 cps, and which was superimposed on a very broad singlet at τ 3.60) and τ 2.63 to τ 1.80 (4.0 H, multiplet).

Anal. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.20.

Found: C, 57.71; H, 5.58; N, 11.12.

22. Ethyl trans-3-(m-Nitrophenyl)-2-propenylnitrosocarbamate. Thirteen and one-half grams (yield 97%) of this compound was prepared from 12.5 g (50 mmoles) of ethyl trans-3-(m-nitrophenyl)-2-propenylcarbamate and 7.5 g (120 mmoles) of nitrosyl chloride in pyridine solution using the procedure described for the preparation of ethyl trans-3-phenyl-2-propenylnitrosocarbamate (Procedure B35). The compound is a yellow crystalline solid (mp 66.5-68.0°) whose infrared and ^{1}H nmr spectra are shown in Figures 21 and 37.

23. trans-3-(p-Chlorophenyl)-2-propenal. Methanolic potassium hydroxide (6 ml of 3N solution) was added to a vigorously stirred solution of 42 g (0.30 mole) of p-chlorobenzaldehyde in 80 ml (62.5 g, 1.5 moles) of acetaldehyde at -5°. After 3.0 min, 80 ml of acetic anhydride was added and the solution was stirred at 80° for 20 min. Then 400 ml of 1 N hydrochloric acid was added and the mixture was refluxed

for 30 min. The mixture was cooled and extracted with two 150-ml portions of ether. The combined organic phase was washed with 5% aqueous sodium bicarbonate solution and water. The ether was stripped from the solution after the solution had been dried over anhydrous magnesium sulfate. The residue was distilled through a 20-cm Vigreaux column. The product (16.3 g, yield 26%) was collected as a yellowish liquid ($bp_{1.0}$ 104-110°) which solidified (mp 46-54°). After being recrystallized from hexane twice, it formed white needles, mp 60-61 (lit. 54, 63-65°) with the following properties: infrared spectrum (CCl_4) 1690(s), 1630(m), 1600(m), 1495(m), 1120(s), 1093(s) and 980(m) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 3.35 (1.0 H, doublet, J=16.1 cps, further split into two doublets, J=7.2 cps), τ 2.55 (doublet, J=16.1 cps, stradling a singlet located at τ 2.55, total 5.0 H) and τ 0.30 (0.9 H, doublet, J=7.2 cps).

24. trans-3-(p-Chlorophenyl)-2-propen-1-ol. Sodium borohydride (1.52 g, 40 mmoles) was slowly added to a stirred solution of 20 g (120 mmoles) of trans-3-(p-chlorophenyl)-2-propenal in 300 ml of ethanol at 25°. The solution was stirred for 48 hr and then 50 ml of 1N hydrochloric acid was slowly added. The ethanol was stripped off and the residue taken up in ether. The ether solution was washed with 5% aqueous sodium bicarbonate and water, dried over anhydrous magnestium sulfate and evaporated to dryness under vacuum. The white solid which remained (18.8 g, mp 46-50°, yield 93%),

when recrystallized from 4:1 hexane-carbon tetrachloride, gave white needles with the following properties: mp 53.5-54.5° (lit. 55 mp 57-58°); infrared spectrum (CCl_4) 3600(m), 3500 (weak and broad), 3030(w), 2875(m), 1600(w), 1495(s), 1380(m), 1090(s) and 975(s) cm^{-1}; ^1H nmr (CCl_4) τ 6.00 (1.0 H, singlet), τ 5.84 (2.0 H, doublet, J=4.3 cps), τ 4.15 to τ 3.37 (2.2 H, an AB quartet, J=16.2 cps, with the high field doublet further split into two triplets, J=4.3 cps) and τ 2.88 (4.0 H, singlet).

25. trans-3-Chloro-1-(p-chlorophenyl)propene. Thionyl chloride (23.8 g, 0.20 mole) was added dropwise to a solution of 16.8 g (0.10 mole) of trans-3-(p-chlorophenyl)-2-propen-1-ol in 75 ml of chloroform at room temperature. A gas evolved. The solution was stirred at 25° for 1 hr and at 55° for 3 hr. After being cooled, the solution was extracted with water, aqueous sodium bicarbonate solution and water, dried over anhydrous magnesium sulfate and evaporated to dryness under vacuum. The oily white solid which remained was dissolved in 25 ml of hexane and the solution was cooled in dry ice. The product (13.3 g, yield 73%) separated as white crystals, mp 42-44°. After a second recrystallization from hexane, the product had the following properties: mp 44-45°; infrared spectrum (CCl_4) 3030(m), 2950(m), 1650(w), 1600(m), 1495(s), 1095(s) and 970(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 5.90 (2.0 H, doublet, J=5.9 cps), τ 4.14 to τ 3.32 (an AB quartet, J=15.2 cps, with the high field doublet

further split into two triplets, J=5.9 cps, total 2.0 H) and τ 2.81 (4.2 H, singlet).

26. N-[*trans*-3-(*p*-Chlorophenyl)-2-propenyl]phthalimide. A slurry of 11.1 g (60 mmoles) of potassium phthalimide and 10.0 g (54 mmoles) of *trans*-3-chloro-1-(*p*-chlorophenyl)propene in 80 ml of dimethylformamide was stirred at room temperature for 15 hr. The reaction mass was poured into 400 ml of water and the slurry filtered. The solid collected was dissolved in 300 ml of hot benzene, the solution dried over anhydrous magnesium sulfate and the volume of the solution reduced to 130 ml. White crystals (12.9 g, yield 81%) precipitated. The product had the following properties: mp 171.5-172.5°; infrared spectrum ($CHCl_3$) 1768(m), 1710(s), 1405(m), 1105(m), and 980(m); ^1H nmr spectrum ($DCCl_3$) τ 5.59 (1.8 H doublet, J=5.6 cps), τ 4.09- τ 3.25 (AB quartet, J=15.4 cps, with the high field doublet split into two triplets, J=5.6 cps, total 2.0 H), τ 2.80 (4.0 H, singlet) and τ 2.23 (4.0 H, multiplet).

27. Hydrochloride of *trans*-3-Amino-1-(*p*-chlorophenyl)-propene. Six grams (yield 70%) of the desired amine hydrochloride was obtained by refluxing a solution of 13.2 g (45 mmoles) of N-[*trans*-3-(*p*-chlorophenyl)-2-propenyl]phthalimide and 4.5 g (90 mmoles) of 99% hydrazine hydrate in 170 ml of methanol for 4.5 hr. The procedure used is the same one described for the preparation of the hydrochloride of *trans*-3-amino-1-phenylpropene (Procedure B33). The product crystallized from water as white plates, mp 241-251° (corrected).

28. Ethyl trans-3-(p-Chlorophenyl)-2-propenylcarbamate. The procedure for this preparation was the one described for the preparation of ethyl trans-3-phenyl-2-propenylcarbamate (Procedure B34). Five and one-half grams of the hydrochloride of trans-3-amino-1-(p-chlorophenyl)propene gave 3.32 g (yield 52%) of the desired product. This compound crystallized from hexane as white blades (mp 89.0-89.5°) and its infrared spectrum (CCl_4) had major bands at 3490(m), 3000(m), 1703(s), 1510(s), 1220(s), 1090(m), and 975(m) cm^{-1}.

29. Ethyl trans-3-(p-Chlorophenyl)-2-propenylnitrosocarbamate. This compound was prepared in 97% yield from ethyl trans-3-(p-chlorophenyl)-2-propenylcarbamate and nitrosyl chloride using the procedure described for the preparation of ethyl trans-3-phenyl-2-propenylnitrosocarbamate (Procedure B35). The product precipitated from a mixture of methanol and water as yellow crystals, mp 57.5-58.5°. The infrared and ^{1}H nmr spectra of this compound are shown in Figures 22 and 38.

30. trans-3-Phenyl-2-propen-1-ol. A solution of 264 g (2.0 moles) of cinnamaldehyde in 500 ml of methanol was cooled in an ice bath. Sodium borohydride (24 g, 0.64 mole) was added in small portions over a 30-min period. The solution was stirred at room temperature for 4 hr and then 400 ml of 10% aqueous sodium hydroxide was added. The solution was refluxed for 2 hr. After 250 ml of methanol was distilled, the residue was poured into 2 liter of water and the

organic phase was taken up in ether. The ether solution was washed with 10% sulfuric acid, 5% sodium bicarbonate and water. The ether was removed after the solution had been dried over anhydrous magnesium sulfate. The residue was distilled through a 20-cm Vigreaux column. Cinnamyl alcohol (187 g, yield 70%) distilled as a clear, colorless liquid, bp_8 122-128°.

31. trans-3-Chloro-1-phenylpropene. The procedure used is described by H. Gilman and S. H. Harris (56). A solution of 202 g (1.7 moles) of thionyl chloride and 142 g (1.8 moles) of pyridine in 140 ml of chloroform was added drop by drop to a stirred solution of 187 g (1.4 moles) of trans-3-phenyl-2-propen-1-ol in 140 ml of chloroform cooled in an ice bath. The addition took 1.5 hr. The solution was refluxed for 1 hr, cooled to room temperature and washed with four 70-ml portions of water. After being dried over anhydrous magnesium sulfate, it was distilled through a 20-cm Vigreaux column. The product (112 g, yield 53%) distilled as a clear, colorless liquid, bp_6 97-100° (lit. 56, bp_6 109-110°).

32. N-(trans-3-Phenyl-2-propenyl)phthalimide. A slurry of 148 g (0.80 mole) of potassium phthalimide and 100 g (0.73 mole) of trans-3-chloro-1-phenylpropene in 800 ml of dimethylformamide was stirred at room temperature for 2.5 hr and then poured into 2 l. of cold water. A white solid separated. It was isolated by filtration and was dissolved in 1.5 liters of chloroform. The solution was washed with

water and dried over anhydrous magnesium sulfate. A white solid which was wet with dimethylformamide was obtained after the chloroform was stripped off. The solid was slurried in 250 ml of cold ether and filtered leaving 162 g (yield 83.5%) of white, crystalline product, mp 150.0-150.7° (lit. 57, mp 153.0-153.5°).

33. Hydrochloride of *trans*-3-Amino-1-phenylpropene. A solution of 160 g (0.60 mole) of N-(*trans*-3-phenyl-2-propenyl)-phthalimide and 60 g (1.20 moles) of 99% hydrazine hydrate in 1.6 liters of methanol was refluxed for 1 hr. The thick white slurry was cooled and 800 ml of concentrated hydrochloric acid was added. After being refluxed for 30 min, the slurry was cooled in an ice bath and was filtered. The solid, white phthalhydrazide which separated was slurried with 200 ml of water and filtered. The filtrates were combined and volume of the solution reduced to 600 ml using a rotary evaporator. The solution was cooled in an ice bath and was filtered, whereupon the product separated as featherlike, white plates. After being dried in air, the white solid weighed 90 g (yield 88%) and had a mp of 215-225° (corrected mp 222-232°), lit. 57, mp 209-219°.

34. Ethyl *trans*-3-Phenyl-2-propenylcarbamate. A solution of 42.3 g (0.25 mole) of the hydrochloride of *trans*-3-amino-1-phenylpropene in 200 ml of water was made strongly basic by slowly adding a solution of 14.6 g (0.37 mole) of sodium hydroxide in 50 ml of water. The mixture was extracted three

times with 50-ml portions of ether and the combined extracts were dried over anhydrous sodium sulfate. This solution of amine was stirred in an ice bath and slowly 27.2 g (0.25 mole) of ethyl chloroformate was added dropwise. When one-half of the ethyl chloroformate had been added, the simultaneous addition of a solution of 10 g (0.25 mole) of sodium hydroxide in 20 ml of water was begun. After the additions were complete, the two phases were separated and the aqueous phase was extracted with 100 ml of ether. The combined organic phase was washed with 1 N hydrochloric acid, 5% sodium bicarbonate solution and water. The solution was dried over anhydrous magnesium sulfate and the ether was removed leaving 43.4 g (yield 85%) of a white crystalline product, mp 51-53°. Recrystallization from 500 ml of hot _n_-hexane gave 35.7 g of white needles, mp 52.5-53.5°. This compound had the following properties: infrared spectrum (CCl_4) 3497(m), 2998(m), 1720(s), 1506(s), 1225(s), 970(m) and 695(m) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 8.82 (3.0 H, triplet, J=7.2 cps), τ 6.17 and τ 5.96 (4.0 H, a triplet overlapping with a quartet, J=5.5 cps and J=7.2 cps respectively), τ 4.45 (0.6 H, very broad singlet), τ 4.29 to τ 3.39 (1.9 H, an AB quartet, J=16 cps, with the high field double further split into two triplets, J=5 cps, and τ 2.78 (5.3 H, singlet).

35. Ethyl _trans_-3-Phenyl-2-propenylnitrosocarbamate. A cold solution of 2.9 g (44 mmoles) of nitrosyl chloride (58) in 6 ml of dry pyridine was added to a solution of 4.1 g

(20 mmoles) of ethyl trans-3-phenyl-2-propenylcarbamate in 30 ml of dry pyricine at -5° under a nitrogen atmosphere. The temperature rose to 11° and some pyridine hydrochloride precipitated. The slurry was stirred at -1° for 15 min, then poured into 300 ml of water. The yellow oil which separated was taken up in ether and the ether solution was washed with 1 N hydrochloric acid, 5% aqueous sodium bicarbonate solution and water. The ether was removed at reduced pressure after the solution had been dried over anhydrous magnesium sulfate. There remained 4.44 g (yield 94%) of a yellow, liquid product. The infrared and ^1H nmr spectra of this compound are shown in Figures 23 and 39.

36. Ethyl trans-3-(p-Tolyl)-2-propenoate. A solution of 93 g (0.71 mole) of ethyl hydrogen malonate, 76.8 g (0.64 mole) of p-tolualdehyde and 13 ml of piperidine in 480 ml of pyridine was stirred on a steam bath for 4 hr, then refluxed for 30 min. The solution was cooled and poured into 500 ml of cold water. Concentrated hydrochloric acid was added until the slurry was acidic and the organic material was taken up in ether. The ether solution was washed with 5% aqueous sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate. After the solvent was removed, the residue was distilled through a 20-cm Vigreaux column. The product (98.6 g, yield 81%) was collected as a clear, colorless liquid, $bp_{2.1}$ 120-123° (lit. 59, bp_{23} 167°). Its infrared spectrum (CCl_4) showed bands at 2980(m), 1710(s), 1640(s), 1305(s),

1170(s) and 1045(m) cm^{-1}. Its ^1H nmr spectrum (CCl_4) showed peaks at τ 8.75 (3.0 H, triplet, J=7.1 cps), τ 7.75 (3.0 H, singlet), τ 5.82 (2.0 H, quartet, J=7.1 cps), τ 3.74 (1.0 H, doublet, J=16 cps), τ 2.85 (4.0 H, AB quartet, J=8 cps) and τ 2.42 (1.1 H, doublet, J=16 cps).

37. trans-3-(p-Tolyl)-2-propen-1-ol. A solution of 108 g (0.57 mole) of ethyl trans-3-(p-tolyl)-2-propenonate in 300 ml of anhydrous ether was slowly added to a stirred slurry of 15.6 g of lithium aluminum hydride in 1 liter of anhydrous ether at -20°. The reaction was carried out under a nitrogen atmosphere. After the addition was completed, the solution was stirred at 25° for 6 hr and then the excess lithium aluminum hydride was destroyed by very carefully adding water drop by drop at -20°. The reaction mixture was warmed to 25° and 800 ml of 10% sulfuric acid was added. The two phases were separated. The ether layer was washed with 5% aqueous sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate. The ether was removed and the white solid which remained was recrystallized from 200 ml of hexane to give 70.3 g (yield 83%) of white crystals, mp 41-45°. After a second recrystallization the mp was 47-48° (lit. 60, mp 50.0-50.3°); infrared spectrum (CCl_4) 3650(m), 3400(m), 3030(m), 2930(m), 2870(m), 1620(m), 1380(m), 1095(s) and 975(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 7.77 (3.0 H, singlet), τ 5.85 (2.7 H, doublet, J=4.2 cps superimposed on a very broad singlet), τ 4.20 to τ 3.22 (an AB quartet, J=16.4 cps, with the high

field doublet further split into two triplets, J=4.2 cps, total 1.6 H) and τ 2.98 (4.0 H, AB quartet, J=7 cps).

38. trans-3-Chloro-1-(p-tolyl)propene. This compound was prepared in 70% yield from trans-3-(p-tolyl)-2-propen-1-ol and thionyl chloride using the procedure described for the preparation of trans-3-chloro-1-(p-chlorophenyl)propene (Procedure B25). The crude product crystallized from hexane as white crystals with the following properties: mp 38-39° (lit. 54, mp 39.5-40.0); infrared spectrum (CCl_4) 3030(m), 2950(m), 1450(m) and 940(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 7.70 (2.9 H, singlet), τ 5.90 (1.9 H, doublet, J=5.8 cps), τ 4.32 to τ 3.30 (AB quartet, J=15.4 cps, with the high field doublet further split into two triplets, J=5.8 cps, total 2.0 H) and τ 2.90 (4.0 H, AB quartet, J=8 cps).

39. N-[trans-3-(p-Tolyl)-2-propenyl]phthalimide. After a slurry of 42.1 g (0.25 mole) of trans-3-chloro-1-(p-tolyl) propene and 51 g (0.28 mole) of potassium phthalimide in 300 ml of dimethylformamide had been stirred for 8 hr at 25°, it was poured into 2 liters of water. The white solid (68.3 g, yield 98%) which precipitated was isolated and dried in air. It had the following properties: mp 165-166°; infrared spectrum (CCl_4) 1770(m), 1720(s), 1430(m), 1395(s) and 1350(m) cm^{-1}; ^1H nmr spectrum ($DCCl_3$) τ 7.74 (3.0 H, singlet), τ 5.60 (1.9 H, doublet, J=5.7 cps), τ 4.20 to τ 3.30 (AB quartet, J=15.4 cps, with the high field doublet further split into two triplets, J=5.7 cps, total 1.8 H), τ 2.87 (4.0 H, AB quartet, J=8.8 cps) and τ 2.27 (4.9 H, multiplet).

40. Hydrochloride of trans-3-Amino-2-(p-tolyl)propene. Thirty-six grams (79% yield) of the desired amine hydrochloride was prepared by refluxing a solution of 68.3 g (0.25 mole) of N-[trans-3-(p-tolyl)-2-propenyl]phthalimide and 25 g (0.50 mole) of 99% hydrazine hydrate in 900 ml of methanol for 4.5 hr. The procedure used is the same as the one described for the preparation of trans-3-amino-1-phenylpropene (Procedure B33). The crude product (35.6 g) was dissolved in 200 ml of hot water. The hot solution was treated with activated charcoal, filtered and cooled. White crystals (33.8 g) separated, mp 236-239° corrected.

41. Ethyl trans-3-(p-Tolyl)-2-propenylcarbamate. This compound was prepared in 85% yield from the hydrochloride of trans-3-amino-1-(p-tolyl)propene and ethyl chloroformate using the procedure which is described for the preparation of ethyl trans-3-phenyl-2-propenylcarbamate (Procedure B34). The product separated from hexane solution as white crystals, mp 61.5-62.5°. Its infrared spectrum (CCl_4) showed bands at 3475(w), 2980(w), 1720(s), 1505(s) and 1220(s) cm^{-1}. Its ^1H nmr (CCl_4) showed peaks at τ 8.85 (3.0 H, triplet, J=7.1 cps), τ 7.75 (3.0 H, singlet), τ 6.22 and τ 5.97 (triplet, J=5.5 cps, overlapping with a quartet, J=7.1 cps, total 4.0 H), τ 4.47 (broad singlet, 1.1 H), τ 4.27 to τ 3.44 (AB quartet, J=15.6 cps, with the high field doublet further split into two triplets, J=5.5 cps, 2.2 H) and τ 2.95 (3.7 H, AB quartet, J=8 cps).

42. Ethyl trans-3-(p-Tolyl)-2-propenylnitrosocarbamate. Nitrosyl chloride (58) (3.3 g, 50 mmoles) was bubbled into a solution of 11.0 g (50 mmoles) of ethyl trans-3-(p-tolyl)-2-propenylcarbamate in 65 ml of dry pyridine which was being stirred at -20° in a nitrogen atmosphere. The solution was stirred at -20° for 1 hr, then poured into 600 ml of water. The yellow oil which separated was taken up in ether and the ether solution was extracted with 1 N hydrochloric acid, 5% aqueous sodium bicarbonate solution and water. After the solution was dried, the solvent was removed at reduced pressure. The crude product, a yellow liquid, was purified by elution from a column of 200 g of silica gel with 1:1 hexane-benzene. The desired product (5.35 g, yield 43%) was the first material to come off of the column. It crystallized from hexane as a yellow solid, mp 44.5-45.0°. The infrared and ^{1}H nmr spectra of this compound are shown in Figures 24 and 40.

C. Preparation and Cyclization of Diazo Compounds

1. 1,3-Bisdiazopropane from N,N'-Trimethylenebis(N-nitrosobenzamide). A slurry of 1.70 g (5.0 mmoles) of N,N'-trimethylenebis(N-nitrosobenzamide) in 40 ml of cyclohexene was cooled to -15° under nitrogen and a solution of 20 mmoles of sodium hydroxide in 7 ml of methanol was added. After being stirred at -15° for 4 hr, the solution was allowed to warm to 0° and quickly extracted with two 40-ml portions of cold

10% aqueous sodium hydroxide solution. The yellow cyclohexene phase was dried over potassium hydroxide pellets at -15° for 30 min. The volume of gas evolved when a sample of this solution was decomposed with acid showed that 1,3-bisdiazopropane was produced in 57% yield (Procedure A7). The infrared spectrum of this solution showed strong absorption bands at 2065 cm^{-1} (diazo group) and 1720 cm^{-1} (methyl benzoate) and its visible spectrum (Figure 6) had a λ max (cyclohexene) at 462 $m\mu$ (ε 27).

2. <u>1,3-Bisdiazopropane from Potassium Propane-1,3-bisdiazotate</u>. Cyclohexene (40 ml) and 1.18 g of crude potassium propane-1,3-bisdiazotate prepared from 5.0 mmoles of N,N'-trimethylenebis(N-nitrosobenzamide) were added to a 100-ml reaction flask. The bisdiazotate was crushed into a fine powder under the cyclohexene. The slurry was cooled to -16° and 7.0 ml of methanol containing 10 mmoles of sodium hydroxide was added. The slurry was stirred in the dark under nitrogen at -16° for 4.75 hr. It was then warmed to 0°, quickly extracted with two 40-ml portions of cold 10% aqueous sodium hydroxide solution and dried over potassium hydroxide pellets for 1 hr at -30°. The infrared spectrum of this clear, yellow cyclohexene solution showed an intense, sharp band at 2065 cm^{-1} (diazo group). The volume of gas evolved when a sample of this solution was decomposed with acid showed that the yield of 1,3-bisdiazopropane based on 5.00 mmoles of potassium propane-1,3-bisdiazotate was 49%.

3. <u>3-Diazopropenes</u>. A solution of 10 mmoles of the appropriate ethyl nitrosocarbamate in 20 ml of cyclohexene was added over a 5-min period to a mixture of 30 ml of cyclohexene and 10 ml of 3 N methanolic sodium methoxide solution (30 mmoles). The mixture was stirred in the dark under nitrogen at +4° (ice bath) for 90 min for all preparations except 3-diazo-1-butene and <u>trans</u>-3-diazo-1-(<u>p</u>-chlorophenyl)-propene. In these preparations stirring times were 30 min and 150 min respectively. The mixture was extracted with two 50-ml portions of cold 10% aqueous sodium hydroxide solution and the clear, red solution of diazo compound in cyclohexene was dried over potassium hydroxide pellets for 10 min at 4°. The yields and references to visible spectra of the diazo compounds are given in Table IX. The yields were determined by measuring the volume of gas evolved when the diazo compounds were decomposed in acid (Procedure A7).

4. <u>Pyrazole from 1,3-Bisdiazopropane</u>. A clear, yellow solution of 19 mmoles of 1,3-bisdiazopropane in 310 ml of cyclohexene was prepared as described in Procedure C2. This solution was allowed to stand in the dark at room temperature for 48 hr. Gas evolved and the yellow color faded. The solution was filtered, removing 0.21 g of a tan solid which burned in a flame but did not melt when heated. Quantitative glc analysis (5-ft, 20% Carbowax 20M on Chromosorb W column at 232° with helium flow of 40 ml/min) of the filtrate using hexamethylbenzene as an internal standard (K=1.01) showed that

Table IX. Yields and Visible Spectra of Diazopropenes

Compound	Percent Yield[a]	Visible Spectrum Figure No.
$CH_2=CHCHN_2$	65	7
$CH_2=C(CH_3)CHN_2$	60	8
$CH_3CH=CHCHN_2$	26	9
$CH_2=CHC(CH_3)N_2$	10	10
m-O_2N-$C_6H_4CH=CHCHN_2$	41	11
p-Cl-$C_6H_4CH=CHCHN_2$	33	12
$C_6H_5CH=CHCHN_2$	16	13
p-Me-$C_6H_4CH=CHCHN_2$	23	14

[a] The yields were determined by measuring the volume of gas evolved when a sample of solution containing the diazo compound was added to acid (Procedure A7).

0.816 g of pyrazole (yield 63%) was produced. The cyclohexene was distilled from the solution through a 45-cm column packed with glass helices. The residue was distilled through a short path column and 0.51 g of pyrazole was collected (bp 170-190^{o}) as a clear, colorless liquid which solidified. This material was recrystallized from hexane and sublimed at 65^{o} and 90 mm to give white needles, mp 66-67^{o} (lit. 61, mp 70^{o}). The melting point of a mixture of this material with an authentic sample of pyrazole was not depressed. The infrared spectrum (Figure 25) and ^{1}H nmr spectrum (Figure 41) were identical with the spectra of an authentic sample of pyrazole. A viscous brown oil (0.59 g) remained in the distillation flask.

5. Pyrazole from 3-Diazopropene. A clear, red solution of 20 mmoles of 3-diazopropene in cyclohexene was allowed to stand in the dark for 48 hr. The red color disappeared. The cyclohexene was distilled through a 40-cm column packed with 0.125-in. glass helices. When the volume of liquid in the distillation pot reached 3 ml, 10 ml of hexane was added and the solution was cooled. Impure pyrazole (0.93 g) separated as oily, yellow crystals which sublimed at 63^{o} and 70 mm, forming white needles (mp 68-70^{o}, lit. 61, mp 70^{o}). The melting point of a mixture of this material and an authentic sample of pyrazole was not depressed. The infrared and ^{1}H nmr spectra of pyrazole are shown in Figures 25 and 41. The yield of pyrazole based on 3-diazopropene was 100%.

This figure was obtained in a separate experiment by determining the amount of 3-diazopropene present in a solution at a particular time (t=0) by measuring the solution's absorbance at 486 mμ (ϵ 19.4). At the same time several drops of acid were added to a known volume of the solution to destroy the 3-diazopropene present. Quantitative glc analysis of this solution gave the amount of pyrazole in the solution at t=0. Similar analysis of the reaction solution after 48 hr at room temperature gave the amount of pyrazole in the solution after all the 3-diazopropene had cyclized. The difference in these two figures was the amount of pyrazole which formed from the 3-diazopropene present at t=0 and was the figure used to calculate the yield. The glc analyses (Procedure A8) used hexamethylbenzene as an internal standard and were carried out at 215° with a helium flow rate of 40 ml/min on a 5-ft column packed with 10% Carbowax 20M on Fluorapak 80.

6. <u>4-Methylpyrazole</u>. After standing in the dark for one week at room temperature, a red solution of 3-diazo-2-methylpropene in cyclohexene became colorless. The cyclohexene was distilled and the liquid residue was analyzed by glc on a 5-ft column packed with 20% Carbowax 20M on Chromosorb W at 220° with a helium flow rate of 20 ml/min. A liquid with a retention time of 8.6 min was collected and was shown to be 4-methylpyrazole. The infrared and ^{1}H nmr spectra of this liquid are reported in Figures 26 and 42 respectively. Cola and Perotti report τ 7.95 and τ 2.85 for the positions of the two high

field singlets of 4-methylpyrazole (62). The picrate of the compound isolated was prepared and recrystallized from water, mp 140-141°. The picrate of 4-methylpyrazole is reported to melt at 142° (63). In a separate experiment the yield of 4-methylpyrazole based on 3-diazo-2-methylpyrazole was found to be 100%. The method used for this determination is described in Procedure C5.

7. <u>3(5)-Methylpyrazole from trans-1-Diazo-2-butene</u>. A red solution of 24 mmoles of *trans*-1-diazo-2-butene in 185 ml of cyclohexene was stored in the dark at room temperature for one week. The red color vanished. The cyclohexene was distilled from the clear, colorless solution and the liquid residue was purified by glc on a 5-ft, 20% Carbowax 20M on Chromosorb W column at 206° (helium flow rate 40ml/min). A liquid with a retention time of 9.1 min was collected. Its infrared spectrum (Figure 27) and ^1H nmr spectrum (Figure 43) are identical with those reported for 3(5)-methylpyrazole (62,64). Quantitative glc analysis of the reaction solution using hexamethylbenzene as an internal standard showed that 1.90 g (yield 109%) of 3(5)-methylpyrazole was produced.

8. <u>3(5)-Methylpyrazole from 3-Diazo-1-butene</u>. A red solution of 3-diazo-1-butene in cyclohexene was stored in the dark at room temperature for 24 hr. The solution became colorless. The cyclohexene was distilled from the reaction mass and the residue was purified by glc on a 5-ft, 20% Carbowax 20M on Chromosorb W column at 240° with a helium flow rate of 40 ml/min. A liquid with retention 6.3 min was

collected. It was identified as 3(5)-methylpyrazole by comparison of its infrared spectrum (Figure 27) with that reported for 3(5)-methylpyrazole (64).

9. 3(5)-(*m*-Nitrophenyl)pyrazole. Using the procedure described for the preparation 3(5)-phenylpyrazole (Procedure C11), 0.26 g of crude 3(5)-(*m*-nitrophenyl)pyrazole was isolated from a solution of 3.5 mmoles of *trans*-3-diazo-1-(*m*-nitrophenyl)propene in 120 ml of cyclohexene. The crude product was recrystallized from a mixture of benzene and hexane and sublimed at 150° and 1 mm to give white crystals, mp 121.0-121.7° (lit. 65, mp 120°). The infrared spectrum (KBr) and ^{1}H nmr spectrum (acetone) are shown in Figure 28 and Figure 44 respectively. The ultraviolet spectrum of this material (3 N HCl) showed a λ max at 250 mμ (ϵ 2.46 x 10^4). In a separate experiment the yield of 3(5)-(*m*-nitrophenyl)-pyrazole based on *trans*-3-diazo-1-(*m*-nitrophenyl)propene was found to be 89%.

10. 3(5)-(*p*-Chlorophenyl)pyrazole. The procedure followed is the one described for 3(5)-phenylpyrazole (Procedure C11). From a solution of about 2 mmoles of *trans*-3-diazo-1-(*p*-chlorophenyl)propene in 40 ml of cyclohexene, 0.21 g of crude 3(5)-(*p*-chlorophenyl)pyrazole was isolated. Recrystallization from 5 ml of hot hexane gave fluffy white crystals, mp 96-97° (lit. 65 mp 98°). The infrared and ^{1}H nmr spectra of this compound are shown in Figures 29 and 45 respectively. Its ultraviolet spectrum (3 N Hcl) showed a λ max at 259 mμ

(ϵ 2.14 x 10^4). In a separate experiment the yield of 3(5)-(p-chlorophenyl)pyrazole based on trans-3-diazo-1-(p-chlorophenyl)propene was found to be 87%.

11. 3(5)-Phenylpyrazole. A red solution of approximately 2 mmoles of trans-3-diazo-1-phenylpropene in 60 ml of cyclohexene was stored in the dark for 48 hr. The red color faded. The light yellow solution was extracted with two 25-ml portions of 3 N hydrochloric acid. The combined extracts were washed with pentane and then made basic by adding solid potassium carbonate. The milky mixture was extracted with four 20-ml portions of ether and the combined ether extracts were dried over anhydrous magnesium sulfate. Removal of the solvent left a liquid which was dissolved in 3 ml of hot 2:1 hexane-benzene. When the solution was cooled, 80 mg of white crystals separated. After a second recrystallization the material was identified as 3(5)-phenylpyrazole, mp 72-73° (lit. 66, mp 78). The melting point of a mixture of this compound and an authentic sample of 3(5)-phenylpyrazole was not depressed. Its infrared spectrum (Figure 30) and ^{1}H nmr spectrum (Figure 46) were identical to those of 3(5)-phenylpyrazole.

The yield of 3(5)-phenylpyrazole based on trans-3-diazo-1-phenylpropene was determined in a separate experiment as follows. The amount of trans-3-diazo-1-phenylpropene present in a cyclohexene solution at a particular time (t=0) was determined by measuring the difference in the absorbance of the solution at 550 mμ (ε 27) at time t=0 and at time t=48 hr. At t=0 several drops of acetic acid were added to an aliquot of this solution thus destroying all of the diazo compound present. The remainder of the solution was allowed to stand in the dark at room temperature until all the diazoalkene was converted to pyrazole (about 48 hr). Then each solution was extracted four times with an equal volume of 3 N hydrochloric acid and the extracts of each combined and washed with pentane. The amount of 3(5)-phenylpyrazole in each aqueous solution was determined by measuring the absorbance of the solutions at 248 mμ. The ultraviolet spectrum of 3(5)-phenylpyrazole in 3 N hydrochloric acid has a maximum at 248 mμ ($\epsilon = 1.42 \times 10^4$). The difference in the amounts of 3(5)-phenylpyrazole found in these two solutions after corrections were made for the differences in their volumes was the amount of 3(5)-phenylpyrazole produced from the trans-3-diazo-1-phenylpropene present at time t=0. The yield calculated from these figures was 86%.

12. 3(5)-(p-Tolyl)pyrazole. The procedure that is described for the preparation 3(5)-phenylpyrazole (Procedure C11) was also used there. Crude 3(5)-(p-tolyl)pyrazole (0.13 g) was isolated from a solution of about 1 mmole of trans-3-diazo-1-(p-tolyl)propene in 30 ml of cyclohexene. The crude product was recrystallized twice from 4:1 hexane-benzene to give white crystals, mp 81.0-81.5° (lit. 67, mp 87-88°). The infrared and ^1H nmr spectra of this compound are shown

in Figures 31 and 47. Its ultraviolet spectrum (3 N HCl) showed a λ max at 260 mμ (ϵ 1.90 x 10^4).

13. Products from the Reactions of Ethyl Allylnitrosocarbamate, Ethyl 2-Methyl-2-propenylnitrosocarbamate, Ethyl *trans*-2-Butenylnitrosocarbamate and Ethyl 1-Methyl-2-propenylnitrosocarbamate with Sodium Methoxide. Approximately 2 mmoles of ethyl alkenylnitrosocarbamate was weighed out to the nearest 0.0001 g and added to a solution of 0.07055 g of methylcyclohexane in 10.0 ml of di-*n*-butyl ether. Then 2.00 ml of 3 N methanolic sodium methoxide solution (6 mmoles) was added and the flask was stoppered, shaken and stored in the dark for 48 hr at room temperature. Ten milliliters of saturated aqueous sodium chloride solution was added and the mixture shaken. The top phase of the two phase system was quantitatively analyzed for ethers by glc on a 10-ft column packed with 20% Carbowax 20M on Chromosorb W at 75° using a helium flow rate of 20 ml/min. Methylcyclohexane was used as the internal standard (Procedure A8). After this was done, 1.0 ml of concentrated hydrochloric acid was added and the mixture was shaken to extract the pyrazole into the aqueous layer. The two layers were separated, 1.00 ml of an aqueous solution containing 0.0640 g of diethylene glycol was added to the aqueous layer and the aqueous layer was made basic by adding solid potassium carbonate. These solutions were quantitatively analyzed for pyrazoles by glc using diethylene glycol as an internal standard. The analyses were

performed on a 5-ft column packed with 10% Carbowax 20M on Fluoropak 80 at 215° (170° for 4-methylpyrazole) with a helium flow rate of 20 ml/min. Table V shows the results of these investigations. The retention times of all the compounds identified were identical with authentic samples of those compounds. The pyrazoles had been isolated and identified as reaction products in earlier experiments (Procedures C5-C8). In separate experiments the ethers were isolated by washing the methanol from the reaction mixture with water, distilling the crude ethers from the higher boiling di-n-butyl ether and purifying the ethers by glc using the conditions mentioned above. The infrared and ^1H nmr spectra of each compound were then compared and found to be identical with those of a sample of the same compound prepared by an alternate route. Allyl methyl ether and 2-methyl-3-methoxypropene were prepared by the reaction of sodium methoxide with allyl chloride and 3-chloro-2-methylpropene respectively. The methyl ethers of trans-2-butenol and 3-hydroxy-1-butene were prepared from the sodium salts of these alcohols and methyl iodide. The infrared and ^1H nmr spectra of these compounds are described below.

Allyl methyl ether: infrared spectrum (CCl_4) 2910(s), 2825(s), 1640(w), 1450(m), 1195(m), 1110(vs), 1007(m) and 915(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 6.75 (2.9 H, singlet), τ 6.18 (2.0 H, doublet, J=5.1 cps, further split into two triplets, J=1.3 cps) and τ 5.07 to τ 3.89 (3.0 H, multiplet).

3-Methoxy-1-butene: infrared spectrum (CCl_4) 2990(s), 2930(s), 1640(w), 1450(s), 1375(s), 1100(vs), 995(m) and 930(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 8.85 (3.0 H, doublet, J=6.5 cps), τ 6.83 (3.0 H, singlet), τ 6.42 (1.2 H, multiplet) and τ 5.15 to τ 4.20 (2.9 H, multiplet).

trans-1-Methoxy-2-butene: infrared spectrum (CCl_4) 2900(s), 1670(w), 1450(s), 1380(s), 1315(s), 1110(s), 1095(s), 975(s) and 920(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 8.32 (3.1 H, doublet, J=5.0 cps, further split), τ 6.80 (3.0 H, singlet), τ 6.24 (1.9 H, multiplet) and τ 4.60 to τ 4.28 (1.9 H, multiplet).

2-Methyl-3-methoxypropene: infrared spectrum (CCl_4) 3000(m), 2925(s), 2810(s), 1655(m), 1455(m), 1190(m), 1100(vs) and 910(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 8.30 (3.0 H, broad singlet), τ 6.74 (3.0 H, singlet), τ 6.26 (2.0 H, broad singlet) and τ 5.14 (2.0 H, multiplet).

The infrared spectrum of butadiene was identical to the reported spectrum (68).

14. Products from the Reactions of Ethyl Cinnamylnitrosocarbamates with Sodium Methoxide. A solution of 5.00 mmoles of the appropriate ethyl cinnamylnitrosocarbamate in 40 ml of cyclohexene was stirred at 4° with 5.0 ml of 3 N methanolic sodium methoxide solution (15 mmoles) for 90 min (150 min for ethyl trans-3-(p-chlorophenyl)-2-propenylnitrosocarbamate). The mixture was extracted twice with 25-ml portions of cold, 10% aqueous sodium hydroxide solution. The reaction flask

was rinsed with 5 ml of cyclohexene and this cyclohexene was used to extract the aqueous phase. The combined organic phase was dried over potassium hydroxide pellets for 10 min, was diluted to 50.00 ml in a volumetric flask and was allowed to stand at room temperature in the dark for 48 hr. A small aliquot of the solution was quantitatively analyzed for ethers by glc using an internal standard (Procedure A8). The glc conditions used for each analysis are given below.

A second aliquot of the reaction solution was extracted four times by an equal volume of 3 N hydrochloric acid. The combined extracts were washed with pentane and after the appropriate dilution with 3 N hydrochloric acid, their ultraviolet spectra were measured. The amount of substituted pyrazole in each sample was calculated from the absorbances measured using the following ϵ values: 3(5)-(m-nitrophenyl) pyrazole, λ max 250 mμ (ϵ 2.46 x 10^4); 3(5)-(p-chlorophenyl) pyrazole, λ max 259 mμ (ϵ 2.14 x 10^4); 3(5)-phenylpyrazole, λ max 248 mμ (ϵ 1.42 x 10^4); 3(5)-(p-tolyl)pyrazole, λ max 260 mμ (ϵ 1.90 x 10^4). In earlier experiments (Procedure C9-C12) each of these pyrazoles had been isolated and identified.

The ethers from each reaction were isolated by removing the solvent from the reaction mixtures after the pyrazoles had been extracted and separating the ethers from the residue by glc. The glc conditions used for these separations and the spectra of the pair of methyl ethers isolated in each experiment are given below.

The following ethers were isolated from the reaction of ethyl trans-3-(m-nitrophenyl)-2-propenylnitrosocarbamate, by glc on a 1.5-ft column packed with 20% SE-30 on Chromosorb W at 180° and with a helium flow rate of 60 ml/min. Triphenylmethane was the internal standard used for the quantitative analysis. 3-Methoxy-3-(m-nitrophenyl)propene: infrared spectrum (CCl_4) 2930(s), 1537(m), 1350(s), 1095(s), 995(m) and 935(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 6.30 (2.8 H, singlet), τ 5.31 (0.9 H, doublet, J=6.2 cps), τ 4.90 to τ 4.11 (3.0 H multiplet) and τ 2.61 to τ 1.80 (4.0 H, multiplet). trans-3-Methoxy-1-(m-nitrophenyl)propene: infrared spectrum (CCl_4) 2920(s), 2825(s), 1660(w), 1535(s), 1452(m), 1350(vs), 1190(s), 1120(vs), 970(s) and 680(m) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 6.32 (3.1 H, singlet), τ 5.98 (2.0 H, doublet), τ 3.97 to τ 3.20 (AB quartet, J=16.4 cps, with the high field doublet further split into two triplets, J=4.4 cps, total 2.0 H), and τ 2.80 to τ 1.88 (4.2 H, multiplet).

The following ethers were isolated from the reaction of ethyl trans-3-(p-chlorophenyl)-2-propenylnitrosocarbamate, by glc on a 1.5-ft column packed with 20% SE-30 on Chromosorb W at 142° with a helium flow rate of 60 ml/min. Fluorene was the internal standard used for the quantitative analysis.

3-Methoxy-3-(p-chlorophenyl)propene: infrared spectrum (CCl_4) 2290(w), 2930(m), 2825(m), 1640(w), 1494(s), 1090(vs), 995(m) and 930(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 6.75 (2.8 H, singlet), τ 5.50 (1.0 H, doublet, J=6.2 cps), τ 5.00 to τ 4.14

(3.2 H, multiplet) and τ 2.79 (4.0 H, singlet).

trans-3-Methoxy-1-(_p_-chlorophenyl)propene: infrared spectrum (CCl_4) 3000(m), 2925(s), 2825(s), 1495(s), 1660(w), 1120(vs), 1090(vs) and 975(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 6.66 (3.0 H, singlet), τ 6.00 (1.9 H, doublet, J=4.6 cps), τ 4.12 to τ 3.29 (AB quartet, J=16.0 cps, with the high field doublet further split into two triplets, J=4.6 cps, total 2.2 H) and τ 2.75 (4.0 H, singlet).

In addition to these two ethers a small amount of _trans_-3-(_p_-chlorophenyl)-2-propen-1-ol was isolated and identified by comparison of its infrared spectrum with that of an authentic sample.

The following ethers were isolated from the reaction of ethyl _trans_-3-phenyl-2-propenylnitrosocarbamate by glc on a 5-ft column packed with 20% Carbowax 20M on Chromosorb W at 200° with a helium flow rate of 56 ml/min. Pentamethylbenzene was the internal standard used for the quantitative analysis.

3-Methoxy-3-phenylpropene: infrared spectrum (CCl_4) 3090(m), 3030(m), 2940(m), 2840(s), 1642(w), 1498(m), 1455(s), 1100(vs), 995(s), 930(s) and 700(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 6.76 (2.9 H, singlet), τ 5.50 (0.9 H, doublet, J=6 cps), τ 5.50 to τ 3.83 (3.4 H, multiplet) and τ 2.79 (5.0 H, singlet). These spectra were identical to those of a sample of this ether prepared from 1-phenyl-2-propen-1-ol and methyl iodide.

trans-3-Methoxy-1-phenylpropene: infrared spectrum (CCl_4) 3050(m), 3000(m), 2920(s), 2820(s), 1655(w), 1605(w), 1498 (m), 1450(s), 1380(s), 1190(s), 1120(vs), 975(s) and 675(s) cm^{-1}; ^1H nmr spectrum (neat) τ 6.88 (2.9 H, singlet), τ 6.15 (1.8 H, doublet, J=4.5 cps), τ 4.18 to τ 3.34 (AB quartet, J=16.0 cps, with the high field doublet further split into two triplets, J=4.5 cps, total 2.0 H) and τ 2.84 (4.0 H, broad singlet). These spectra were identical with those of a sample of the same ether prepared from cinnamyl chloride and sodium methoxide.

The following ethers were isolated from the reaction of ethyl trans-3-(p-tolyl)-2-propenylnitrosocarbamate, by glc on a 5-ft column packed with 20% SE-30 on Chromosorb W at 190° with a helium flow rate of 40 ml/min. Hexamethylbenzene was the internal standard used in the quantitative analysis.

3-Methoxy-3-(p-tolyl)propene: infrared spectrum (CCl_4) 3000(s), 2930(s), 1644(w), 1450(m), 1420(m), 1095(vs), 996(m), and 930(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 7.70 (3.0 H, singlet), τ 6.78 (3.0 H, singlet), τ 5.56 (1.0 H, doublet, J=6 cps), τ 5.09 to τ 3.93 (3.0 H, multiplet) and τ 2.94 (4.0 H, singlet).

trans-3-Methoxy-1-(p-tolyl)propene: infrared spectrum (CCl_4) 3000(s), 2930(s), 1657(w), 1450(m), 1380(m), 1120(vs) and 975(s) cm^{-1}; ^1H nmr spectrum (CCl_4) τ 7.75 (3.2 H, singlet), τ 6.76 (3.0 H, singlet), τ 6.05 (2.0 H, doublet, J=5.0 cps), τ 4.69 to τ 3.35 (AB quartet, J=15.8 cps, with the high field doublet further split into two triplets, J=5.0 cps, total 2.0 H) and τ 2.94 (4.1 H, AB quartet, J=8 cps).

The results of this experiment are given in Table VI.

D. Kinetic Experiments

1. Rate of Formation of Pyrazole from 1,3-Bisdiazopropane. Hexamethylbenzene (0.1228 g) was dissolved in a cyclohexene solution of 1,3-bisdiazopropane which had been prepared from potassium propane-1,3-bisdiazotate. The solution was poured into a black bottle which was clamped in a constant temperature bath at 25.0°. At various time intervals a 1.00-ml sample of the yellow solution was removed and added to a vial containing one drop of acetic acid. The acid destroyed any diazo compound present. The samples were analyzed for pyrazole by glc using hexamethylbenzene as an internal standard. The analyses were carried out on a 5-ft column packed with 10% Carbowax 20M on Fluoropak 80 at 215° with a helium flow rate of 20 ml/min. At the time the first sample was withdrawn there was 2.69 mmoles of 1,3-bisdiazopropane in the solution (40.5 ml). This figure was obtained by measuring the absorbance of the solution at 462 mμ ($\epsilon = 27.4$). The increase in the amount of pyrazole in each sample over the amount present in the first sample is given in Table X. These data are plotted against time in Figure 1.

2. Rates of Cyclization of Diazoalkenes. The rate of disappearance of diazoalkene was obtained by following the decrease of absorbance at a selected wavelength in the visible spectrum of the compound. A cyclohexene solution of diazoalkene in a black bottle was placed in a constant temperature bath at 25.0°. After the temperature had equilibrated,

Table X. Rate Data for the Production of Pyrazole from 1,3-Bisdiazopropane in Cyclohexene Solution at 25.0°

Time (hr)	Δ mmoles pyrazole	Time (hr)	Δ mmoles pyrazole
0.00	0.00	4.10	1.04
0.50	0.17	5.10	1.10
1.00	0.33	6.10	1.19
1.50	0.52	7.10	1.27
2.00	0.65	9.37	1.33
2.50	0.79	25.00	1.32
3.33	0.94		

samples were removed at specified time intervals and the absorbance of the sample was quickly measured at the selected wavelength. The absorbance was measured on a Beckman DB spectrophotometer using 0.996-cm Corex cells. The sample cell was cleaned and the 100% adjustment reset before each measurement. The kinetic data for all the diazoalkenes are given in Tables XI through XVIII. The data for each compound fit the first order rate equation,

$$\log (A-A_{\infty}) - \log (A_o-A_{\infty}) = \frac{-kt}{2.303}$$

where k is the first order rate constant, A the absorbance at time t, A_o the absorbance at t=0 and A_{∞} the absorbance at $t=\infty$ (3 or 4 days). Plots of log $(A-A_{\infty})$ versus t (Figures 2 and 3) are all straight lines from whose slopes the rate constants, k, were calculated using the following equation:

$$k = (-2.303)(\text{slope})$$

trans-3-Diazo-1-(p-tolyl)propene is very sensitive to light and good kinetic data for this compound were obtained only when special precautions were taken to keep the compound away from light. The run was carried out at night in a dark laboratory. Samples were removed from the black bottle and the bottle was capped as quickly as possible. After each measurement, the sample was discarded instead of being returned to the bottle.

The solution of 3-diazo-1-butene was contaminated with _trans_-1-diazo-2-butene. A plot of log $(A-A_{\infty})$ versus t for this compound gave a curved line (Figure 5) which could be resolved (Table XIV) into two straight lines. From the slope of one, a rate constant of 4.51×10^{-5} sec^{-1} was calculated. This agreed well with a value of 4.51×10^{-5} sec^{-1} determined independently for the rate of disappearance of _trans_-1-diazo-2-butene. From the other line the rate constant (7.85×10^{-4} sec^{-1}) for the disappearance of 3-diazo-1-butene was calculated. From the initial absorbance due to _trans_-1-diazo-2-butene (0.091), the yield of this diazo compound from its precusor (33%), the volume of the solution (40 ml) and the amount of ethyl 1-methyl-2-propenylnitrosocarbamate used to prepare the solution (20 mmoles), it was calculated that the precursor to 3-diazo-1-butene was contaminated with 3% of ethyl _trans_-2-butenylnitrosocarbamate.

The rate of cyclization of 3-diazopropene was determined three times to test the precision of the method. Values for the rate constant observed were 6.00, 6.03 and 6.08 x 10^{-5} sec^{-1}. The average deviation is 0.03×10^{-5} sec^{-1}.

Figure 5. Rate of diasppearance of 3-diazo-1-butene and <u>trans</u>-1-diazo-2-butene from a mixture in cyclohexene at 25.0°.

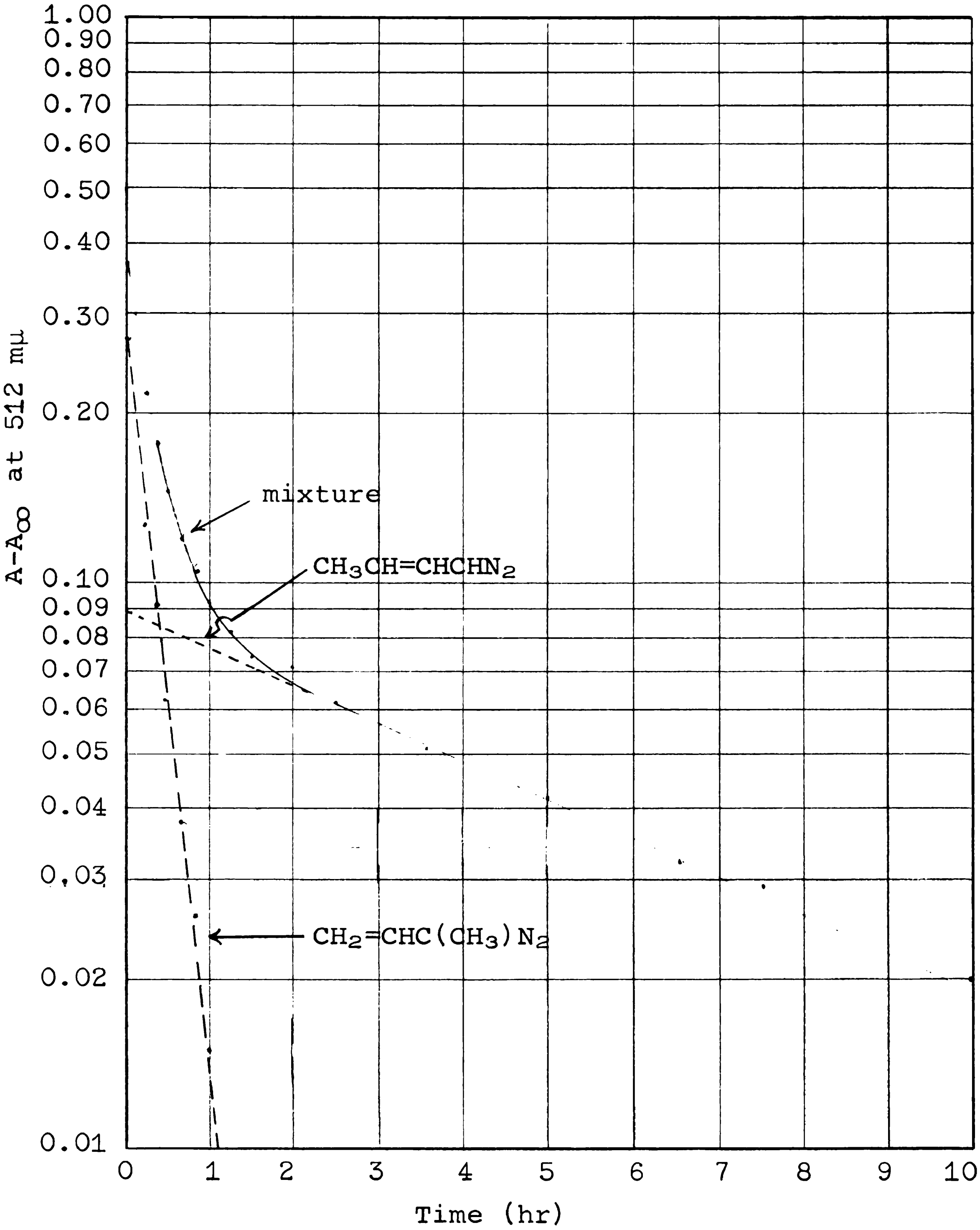


Table XI. Rate Data[a] for the Disappearance of 3-Diazopropene from Cyclohexene Solution at 25.0°.

Time (hr)	$A-A_{\infty}$ (486 mμ)	Time (hr)	$A-A_{\infty}$ (486 mμ)
0.00	0.980	4.25	0.388
0.50	0.880	5.00	0.329
1.00	0.782	6.33	0.247
1.50	0.700	7.92	0.173
2.00	0.630	9.67	0.121
2.75	0.535	10.00	0.112
3.50	0.455		

[a] Rate constant = 6.30×10^{-5} sec^{-1}.

Table XII. Rate[a] Data for the Disappearance of 3-Diazo-2-methylpropene from Cyclohexene Solution at 25.0°

Time (hr)	$A-A_\infty$ (492 mμ)	Time (hr)	$A-A_\infty$ (492 mμ)
0.00	0.830	3.50	0.430
0.50	0.755	4.00	0.397
1.00	0.695	4.50	0.361
1.50	0.633	5.02	0.327
2.00	0.577	5.50	0.300
2.50	0.522	6.50	0.248
3.00	0.476		

[a] Rate constant = 5.15×10^{-5} $\sec^{-1}$.

Table XIII. Rate[a] Data for the Disappearance of *trans*-1-Diazo-2-butene from Cyclohexene Solution at 25.0°

Time (hr)	$A-A_\infty$ (502 mμ)	Time (hr)	$A-A_\infty$ (502 mμ)
0.00	0.905	4.25	0.453
0.50	0.835	5.25	0.386
1.00	0.770	6.50	0.314
1.75	0.680	8.50	0.228
2.50	0.600	9.25	0.202
3.25	0.531	10.00	0.178

[a] Rate constant = 4.51×10^{-5} sec^{-1}.

Table XIV. Rate[a] Data for the Disappearance of 3-Diazo-1-butene and *trans*-1-Diazo-2-butene from a Mixture in Cyclohexene Solution at 25.0°

Time (hr)	$A-A_{\infty}$ (512 mμ)	B (512mμ)[b]	$(A-A_{\infty})-B$ (512 mμ)
0.00	0.361	0.091	0.270
0.25	0.215	0.088	0.127
0.37	0.178	0.086	0.092
0.50	0.146	0.084	0.062
0.67	0.120	0.082	0.038
0.83	0.105	0.079	0.026
1.00	0.093	0.078	0.015
1.25	0.083	-	-
1.50	0.075	-	-
2.00	0.071	-	-
2.50	0.062	-	-
3.58	0.051	-	-
5.00	0.042	-	-
6.50	0.032	-	-
7.50	0.029	-	-
10.00	0.020	-	-

[a] The rate constant for the disappearance of 3-diazo-1-butene is 7.85×10^{-4} sec^{-1}.

[b] Absorbance at 512 mμ due to *trans*-1-diazo-2-butene.

Table XV. Rate[a] Data for the Disappearance of *trans*-3-Diazo-1-(*m*-nitrophenyl)propene from Cyclohexene Solution at 25.0°

Time (min)	$A-A_{\infty}$ (550 mμ)	Time (min)	$A-A_{\infty}$ (550 mμ)
0	0.643	90	0.228
15	0.543	105	0.190
30	0.457	120	0.162
45	0.383	135	0.134
60	0.325	150	0.113
75	0.269	165	0.096

[a] Rate constant = 1.93×10^{-4} sec^{-1}.

Table XVI. Rate[a] Data for the Disappearance of *trans*-3-Diazo-1-(*p*-chlorophenyl)propene from Cyclohexene Solution at 25.0°

Time (min)	$A-A_{\infty}$ (550 mμ)	Time (min)	$A-A_{\infty}$ (550 mμ)
1	0.764	75	0.191
15	0.582	90	0.144
30	0.444	105	0.109
45	0.333	120	0.082
60	0.251		

[a] Rate constant = 3.12×10^{-4} sec^{-1}.

Table XVII. Rate[a] Data for the Disappearance of *trans*-3-Diazo-1-phenylpropene from Cyclohexene Solution at 25.0°

Time (min)	$A-A_\infty$ (550 mμ)	Time (min)	$A-A_\infty$ (550 mμ)
0	0.584	75	0.114
15	0.423	90	0.080
30	0.303	105	0.060
45	0.219	195	0.006
60	0.158		

[a] Rate constant = 3.64×10^{-4} sec^{-1}.

Table XVIII. Rate[a] Data for the Disappearance of *trans*-3-Diazo-1-(*p*-tolyl)propene from Cyclohexene Solution at 25.0°

Time (min)	$A-A_{\infty}$ (550 mμ)	Time (min)	$A-A_{\infty}$ (550 mμ)
0	0.501	50	0.133
15	0.331	65	0.097
25	0.255	80	0.069
35	0.196		

[a] Rate constant = 4.43×10^{-4} sec^{-1}.

E. Miscellaneous

1. 1,5-Diphenyl-1,5-pentanedione from 1,3-Bisdiazopropane. A solution of 2.1 g (20 mmoles) of freshly distilled benzaldehyde in 10 ml of cyclohexene was added to a solution of 3.6 mmoles of 1,3-bisdiazopropane in 36 ml of cyclohexene at -22°. The solution was stirred for 16 hr with the temperature gradually being increased to +5°. The solvent was removed and the residue was distilled through a short path column. The excess benzaldehyde was removed at atmospheric pressure and the product, 0.35 g of 1,5-diphenyl-1,5-pentanedione, was collected at reduced pressure, $bp_{0.1}$ 164°. After being recrystallized from methanol-water, the product had a corrected mp of 66.0-67.0° (lit. 69, mp 67.5°). The dioxime derivative of this diketone precipitated from methanol as white crystals, corrected mp 164-165° (lit. 69, mp 165-166°).

2. 1,5-Diphenyl-1,5-pentanedione from Potassium Propane-1,3-bisdiazotate. Potassium propane-1,3-bisdiazotate (1.13 g) was quickly powdered in air and stirred under nitrogen with 40 ml of cyclohexene, 2.12 g (0.020 mole) of freshly distilled benzaldehyde, and 7.0 ml of methanol containing 0.010 mole of sodium hydroxide. The slurry was stirred for 16 hr starting at -22°. The temperature was slowly increased to +12°. Water (30 ml) was added and the two phases were separated. The aqueous phase was extracted with ether and the extracts were combined with the cyclohexene phase. The combined organic phase was washed with 5% hydrochloric acid, 5%

sodium bicarbonate and water. After the solution was dried over anhydrous magnesium sulfate, the liquid was distilled through a short path head. 1,5-Diphenyl-1,5-pentanedione (0.61 g, $bp_{0.3}$ 171-189°) was collected as an oily white solid which, after recrystallization from methanol, had a mp of 65.5-66.0° (lit. 69, mp 67.5°). The mp of a mixture of this material and an authentic sample of 1,5-diphenyl-1,5-pentanedione was not depressed. The yield based on the bis-diazotate was 52%.

3. <u>1,5-Di-(p-nitrophenyl)-1,5-pentanedione</u>. A solution of 0.88 g (5.8 mmoles) of p-nitrobenzaldehyde in 10 ml of dry tetrahydrofuran was added to a solution of 2.7 mmoles of 1,3-bisdiazopropane in 28 ml of cyclohexene at -21°. The solution was stirred for 9 hr. The temperature gradually increased to 12°. A cream-colored solid separated. The solvent was removed and the oily solid remaining was slurried with 3 ml of ether and filtered. The solid was recrystallized from hot benzene; 0.35 g of product having the following properties was collected: cream-colored crystals; mp 151.5-152.0°; infrared spectrum (KBr) 3075(w), 2920(w), 1695(s), 1685(s), 1603(m), 1526(s), 1351(s), 864(m), 850(m) and 735(m) cm^{-1}; ^1H nmr spectrum ($DCCl_3$) τ 7.57 (2 H, quintet, J=6.8 cps), τ 6.67 (4 H, triplet, J=6.8 cps) and τ 1.78 (8 H, AB quartet). <u>Anal</u>. Calcd for $C_{17}H_{14}N_2O_6$: C, 59.55; H, 4.12; N, 8.18. Found: C, 59.53; H, 4.23; N, 8.16.

IV. SPECTRA

Figure 6. Visible spectrum of 1,3-bisdiazopropane in cyclohexene.

Cells	0.996-cm Corex
λmax	462 mμ (ε = 27.4)

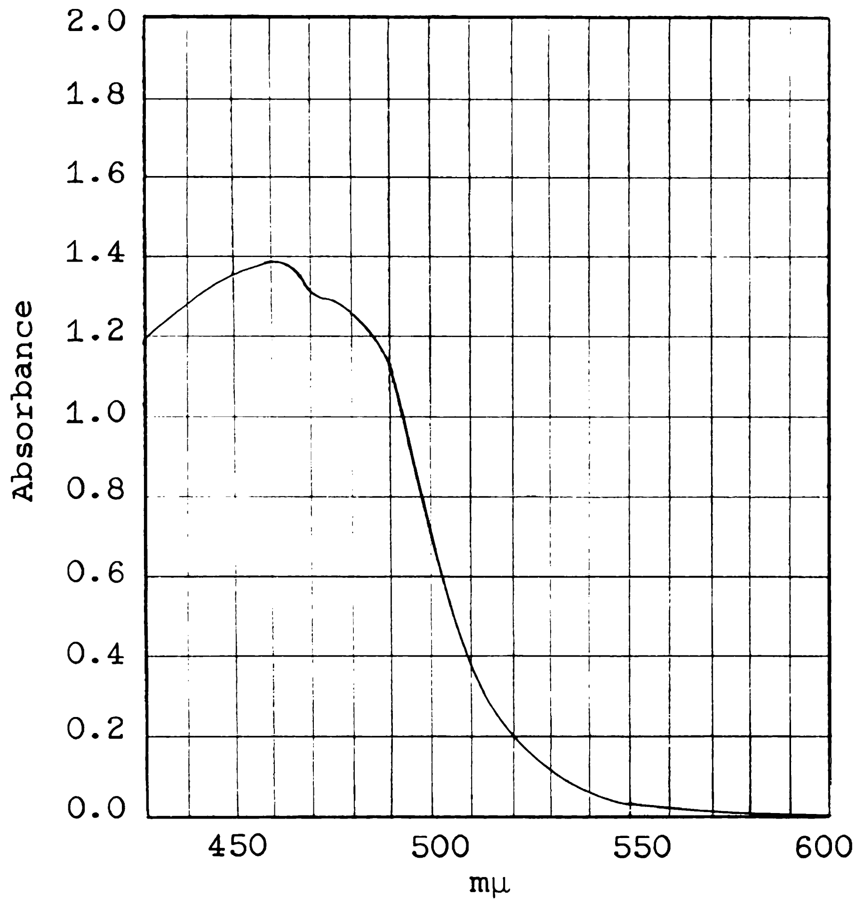


Figure 7. Visible spectrum of 3-diazopropene in cyclohexene.

Cells	0.996-cm Corex
λmax	486 mμ (ε = 19.4)

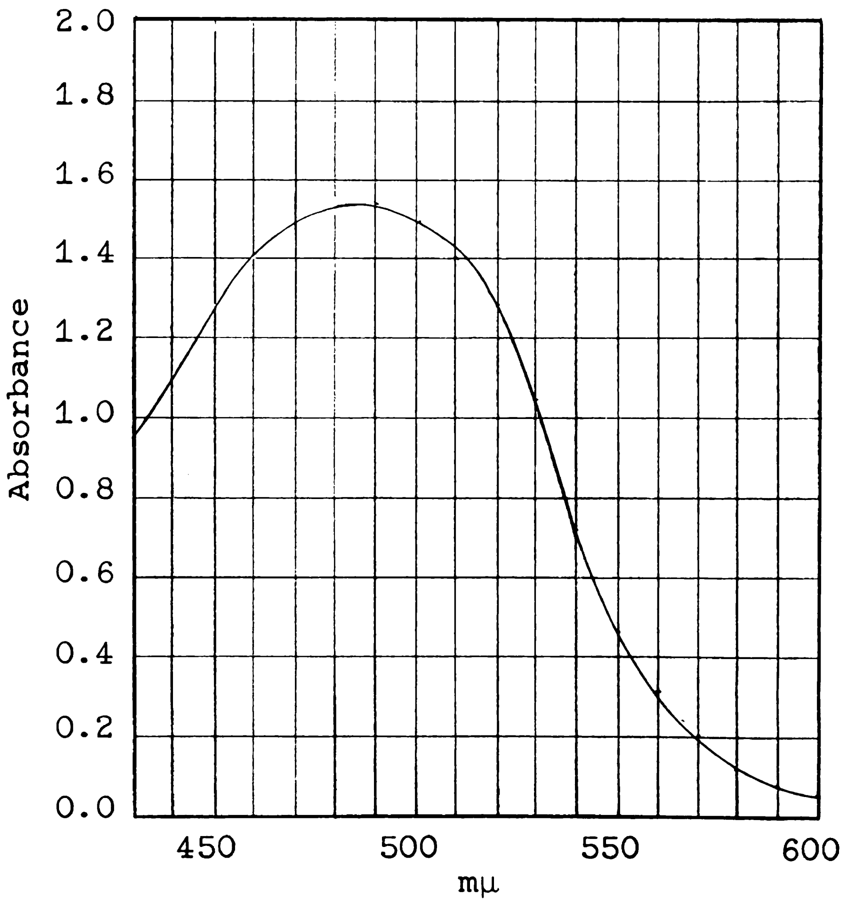


Figure 8. Visible spectrum of 3-diazo-2-methylpropene in cyclohexene

Cells 0.996-cm Corex
λmax 492 mμ (ϵ = 19.2)

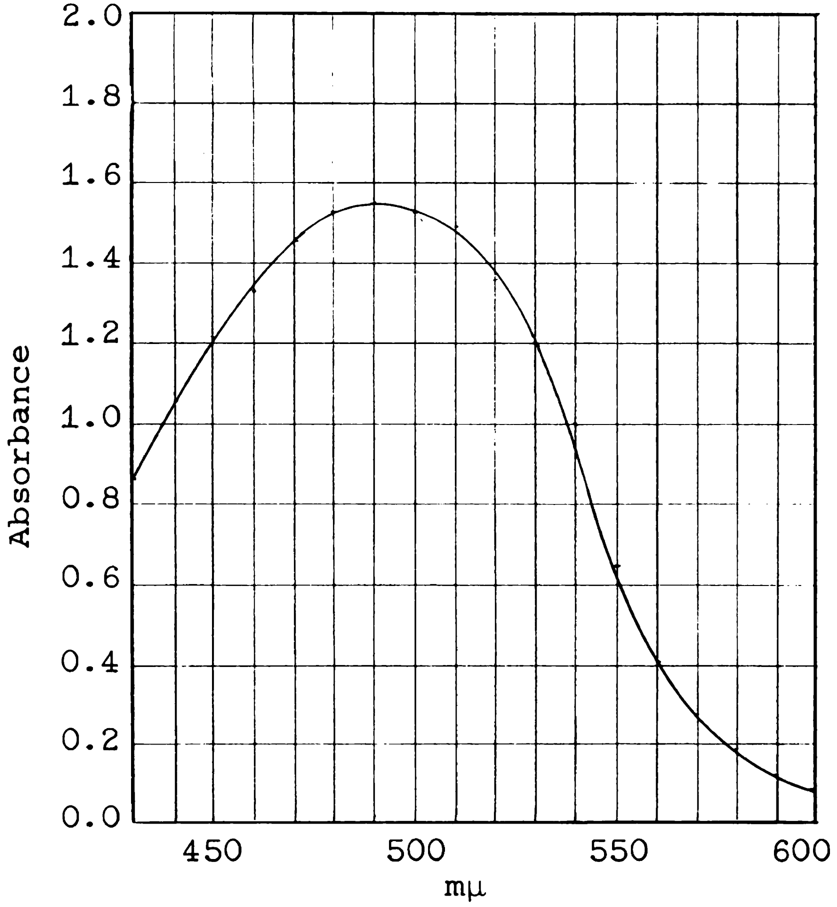


Figure 9. Visible spectrum of *trans*-1-diazo-2-butene in cyclohexene.

Cells 0.996-cm Corex
λmax 502 mμ (ϵ = 24.2)

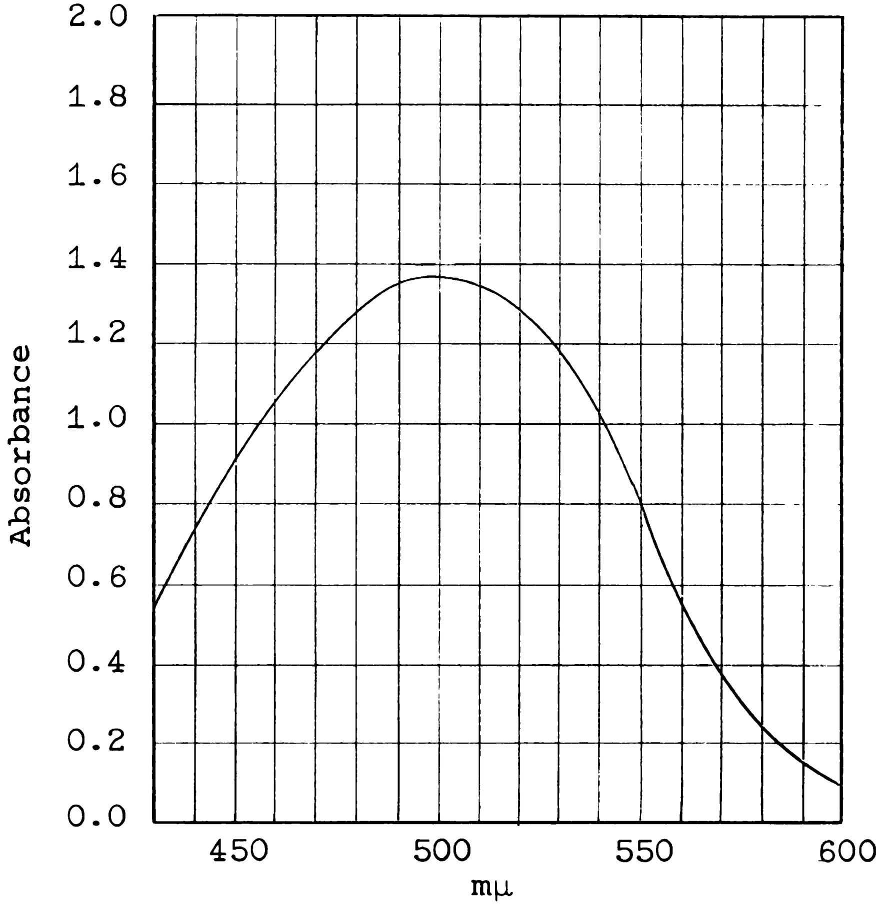


Figure 10. Visible spectrum of 3-diazo-1-butene in cyclohexene.

Cells 0.996-cm Corex
λmax 512 mμ

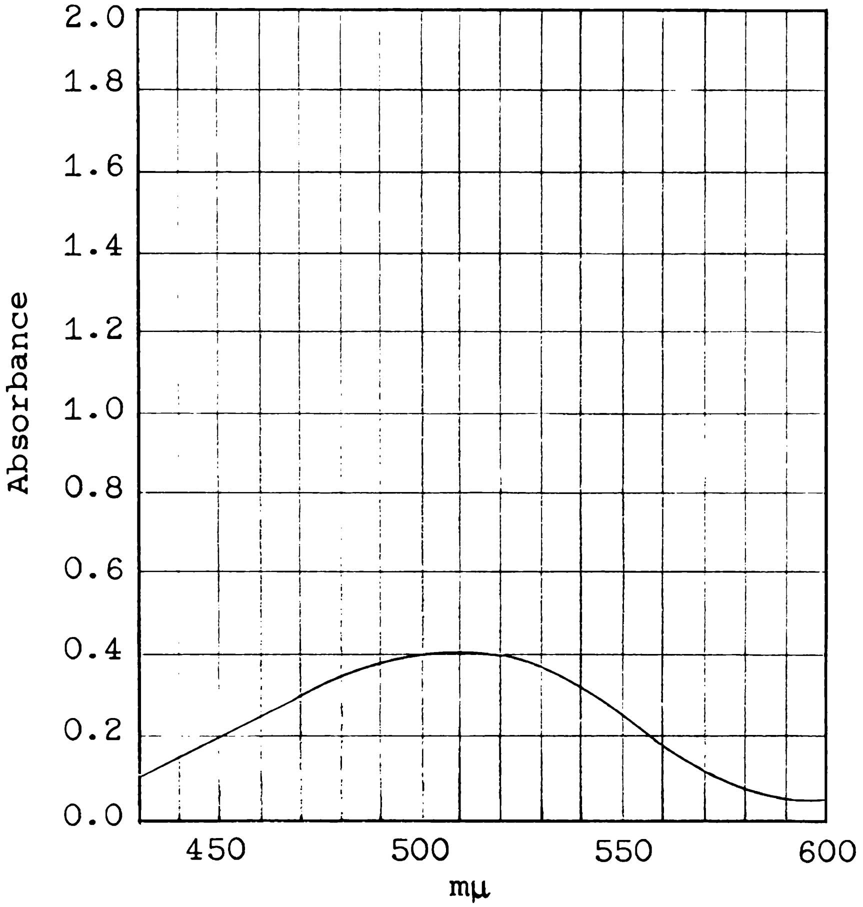


Figure 11. Visible spectrum of *trans*-3-diazo-1-(*m*-nitrophenyl)propene in cyclohexene.

Cells 0.996-cm Corex
λmax 490 mμ (ϵ = 56)

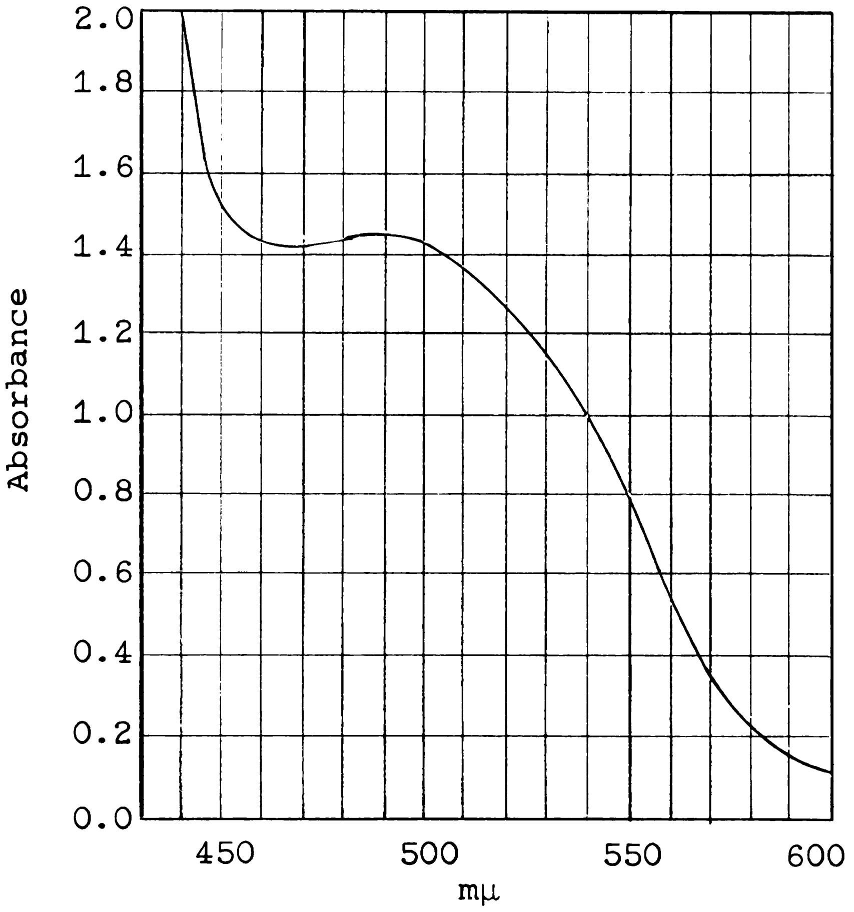


Figure 12. Visible spectrum of <u>trans</u>-3-diazo-1-(<u>p</u>-chlorophenyl)-propene in cyclohexene.

Cells 0.996-cm Corex
$\epsilon_{500} = 64$

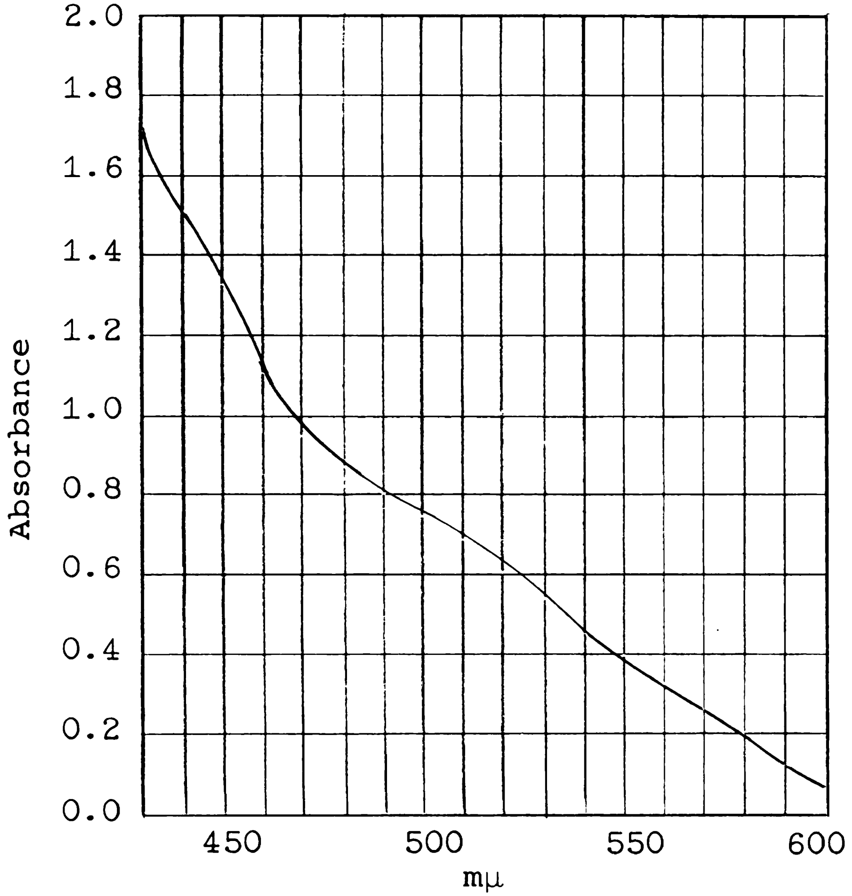


Figure 13. Visible spectrum of <u>trans</u>-3-diazo-1-phenylpropene in cyclohexene.

Cells 0.996-cm Corex
λmax 504 mμ (ϵ = 38)

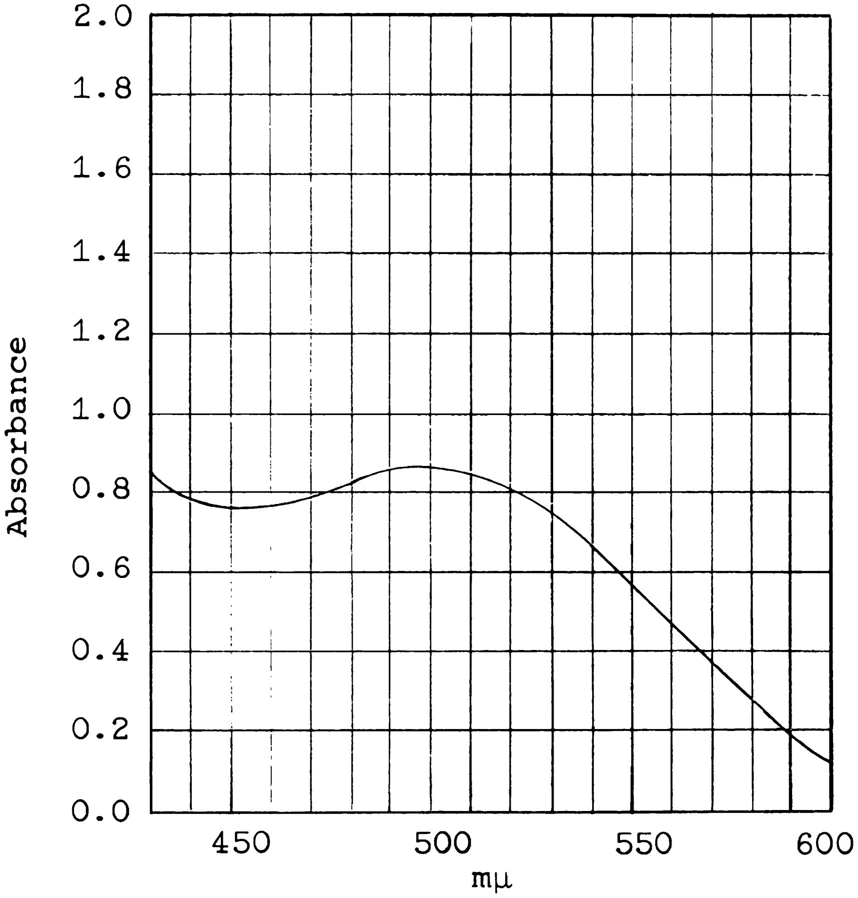


Figure 14. Visible spectrum of *trans*-3-diazo-1-(*p*-tolyl)propene in cyclohexene.

Cells	0.996-cm Corex
ε	not determined

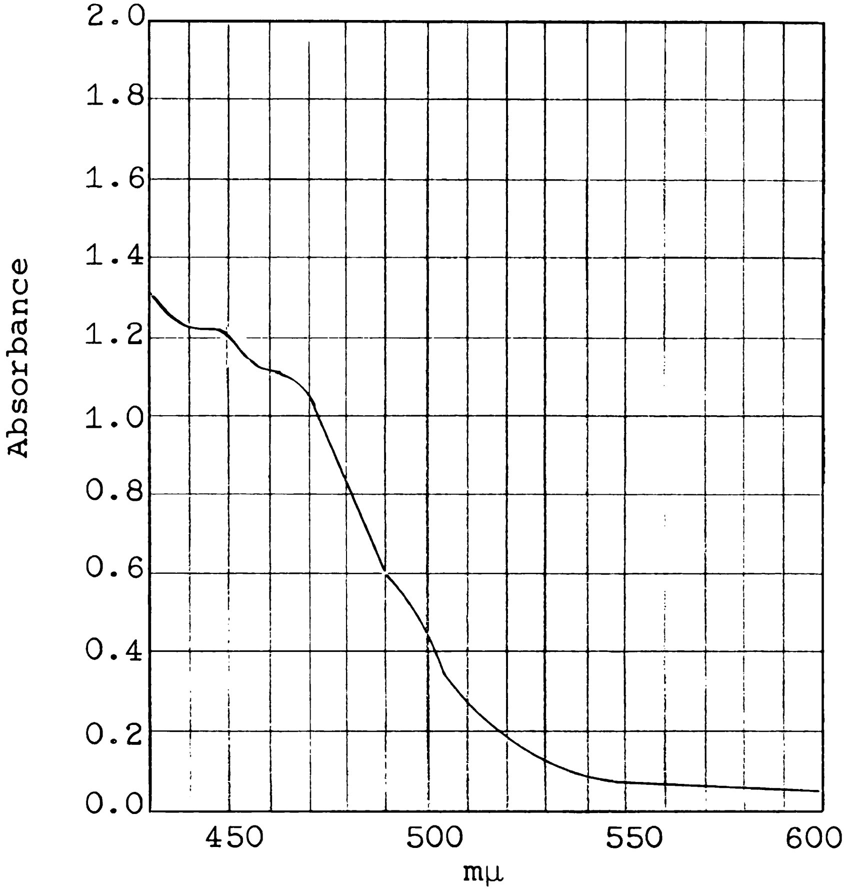


Figure 15. Infrared spectrum of N,N'-trimethylenebis(N-nitrosobenzamide) (CCl_4).

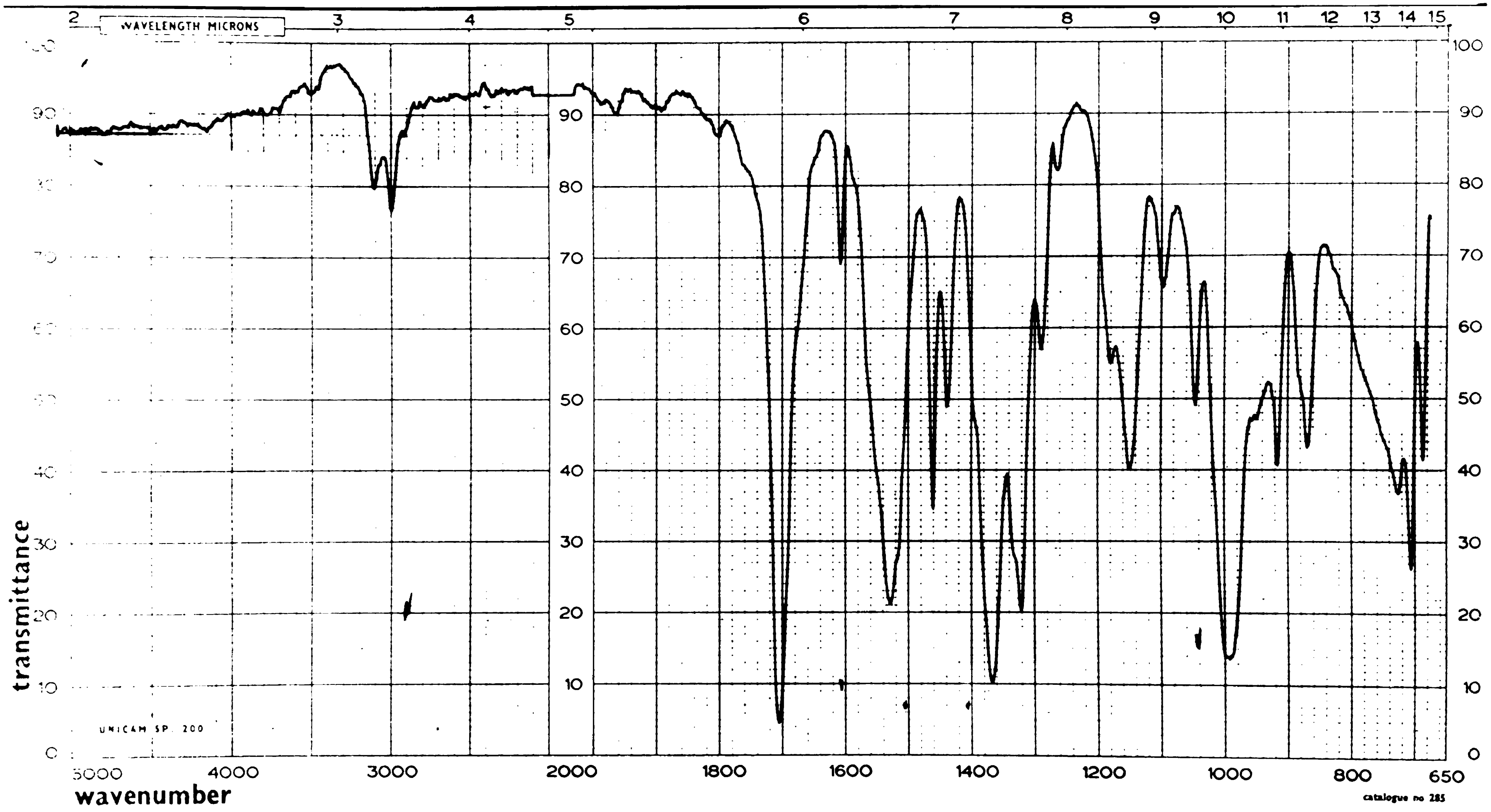


Figure 16. Composite infrared spectrum of potassium propane-1,3-bisdiazotate in Fluorolube and Nujol Mulls.

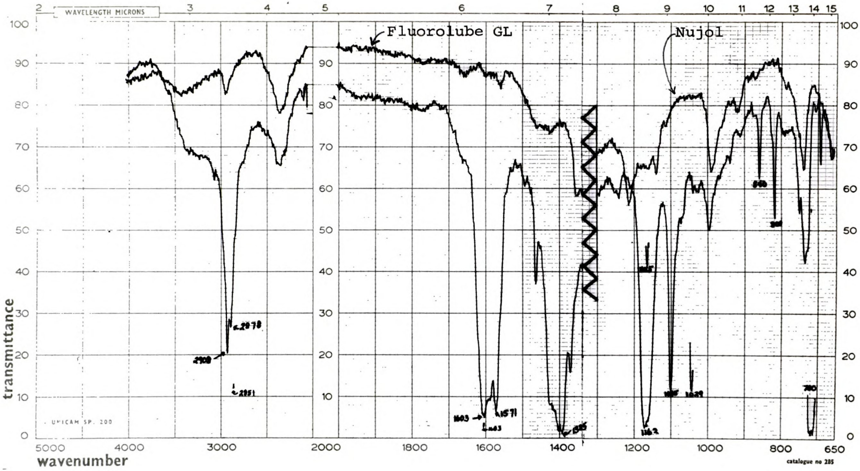


Figure 17. Infrared spectrum of ethyl allylnitrosocarbamate (CCl_4).

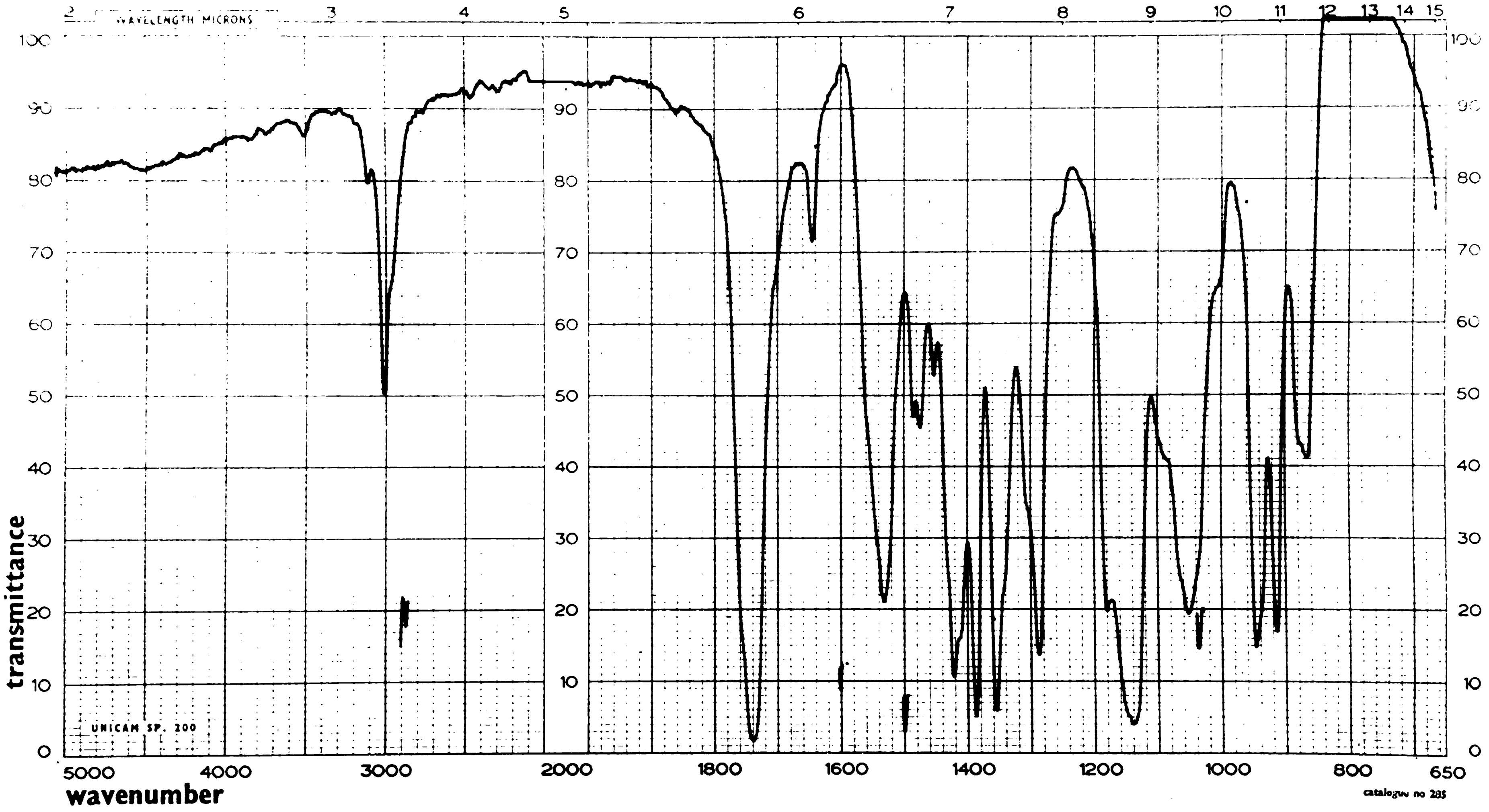


Figure 18. Infrared spectrum of ethyl 2-methyl-2-propenylnitrosocarbamate (CCl_4).

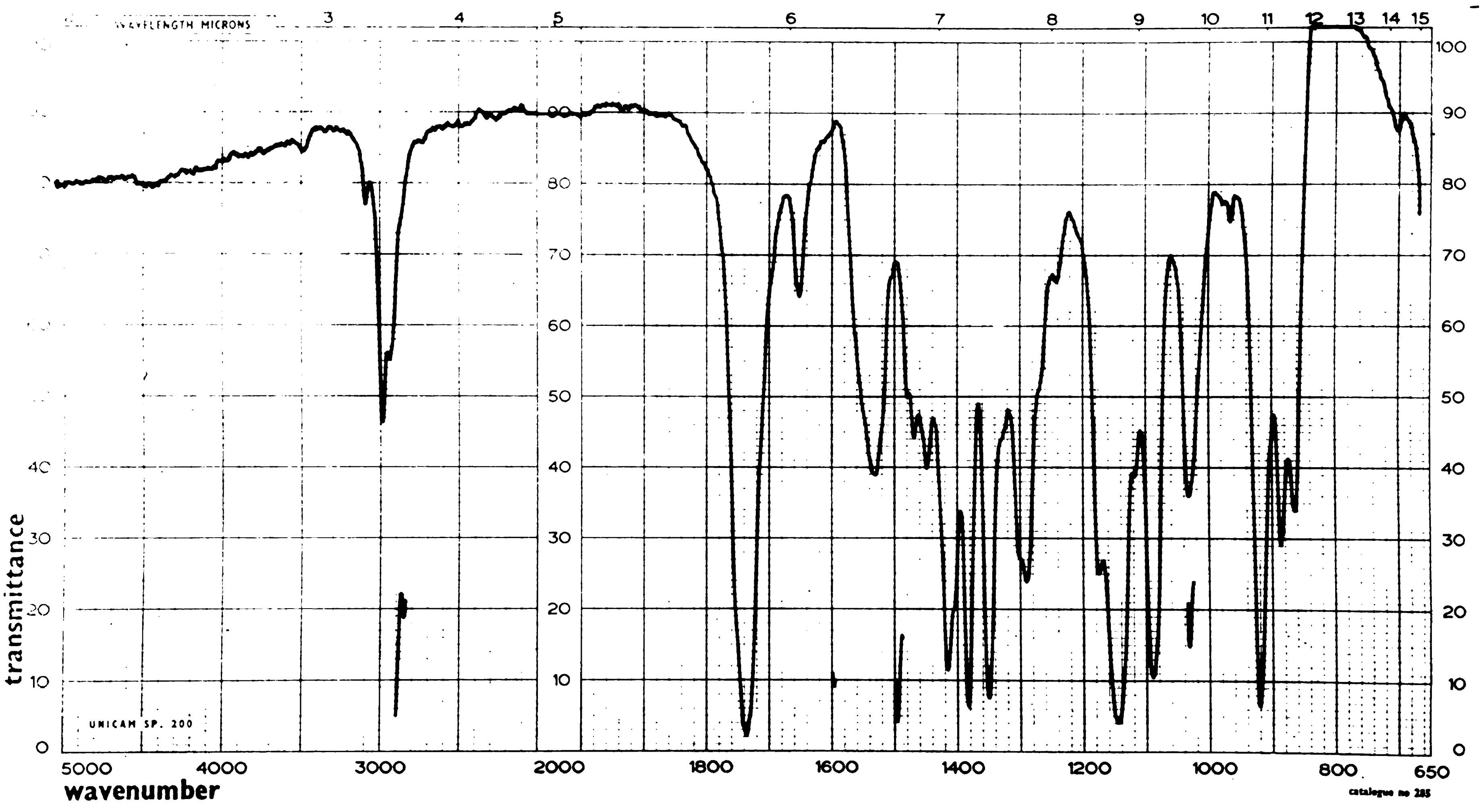


Figure 19. Infrared spectrum of ethyl trans-2-butenylnitrosocarbamate (CCl_4).

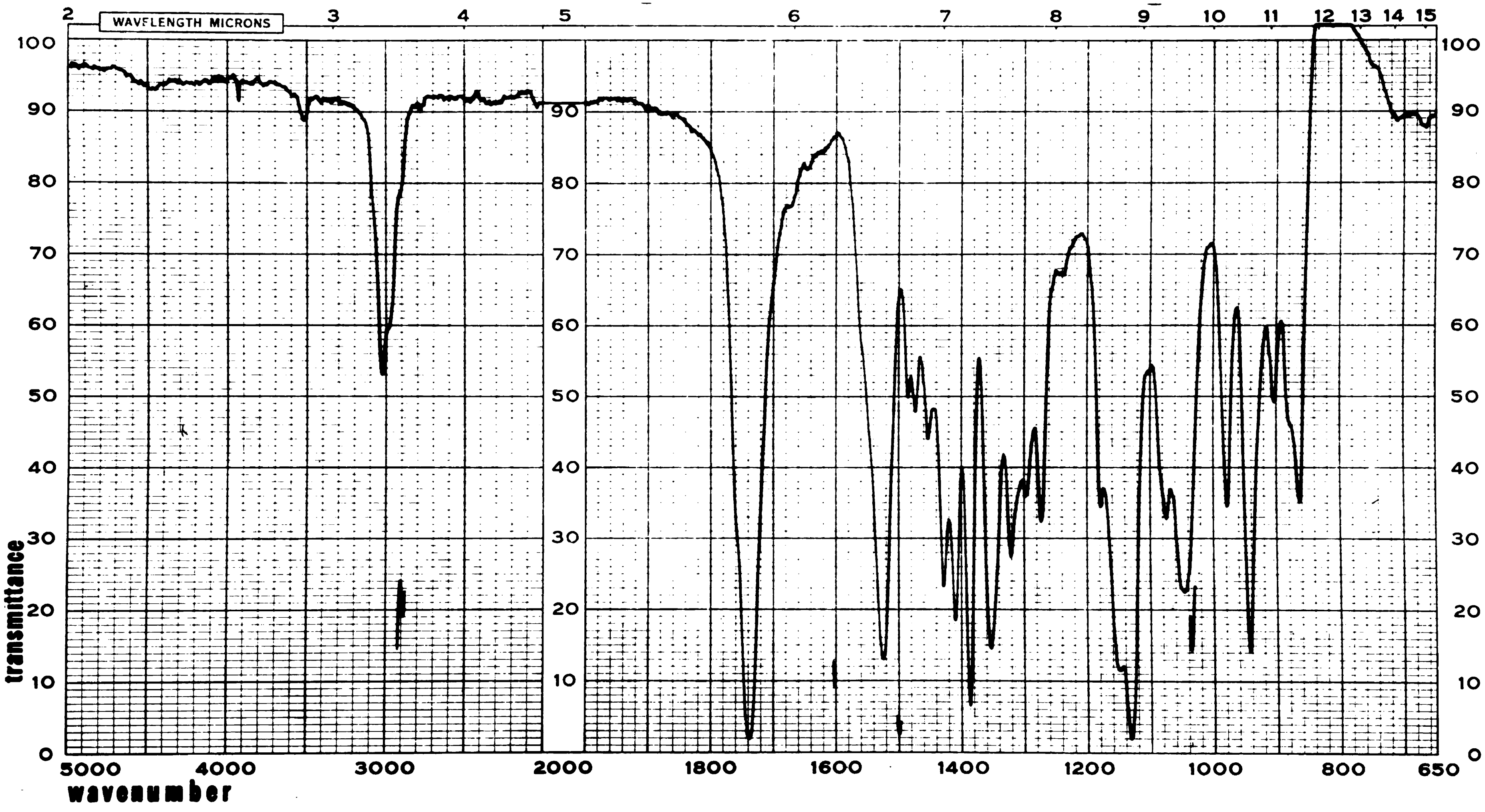


Figure 20. Infrared spectrum of ethyl 1-methyl-2-propenylnitrosocarbamate (CCl_4).

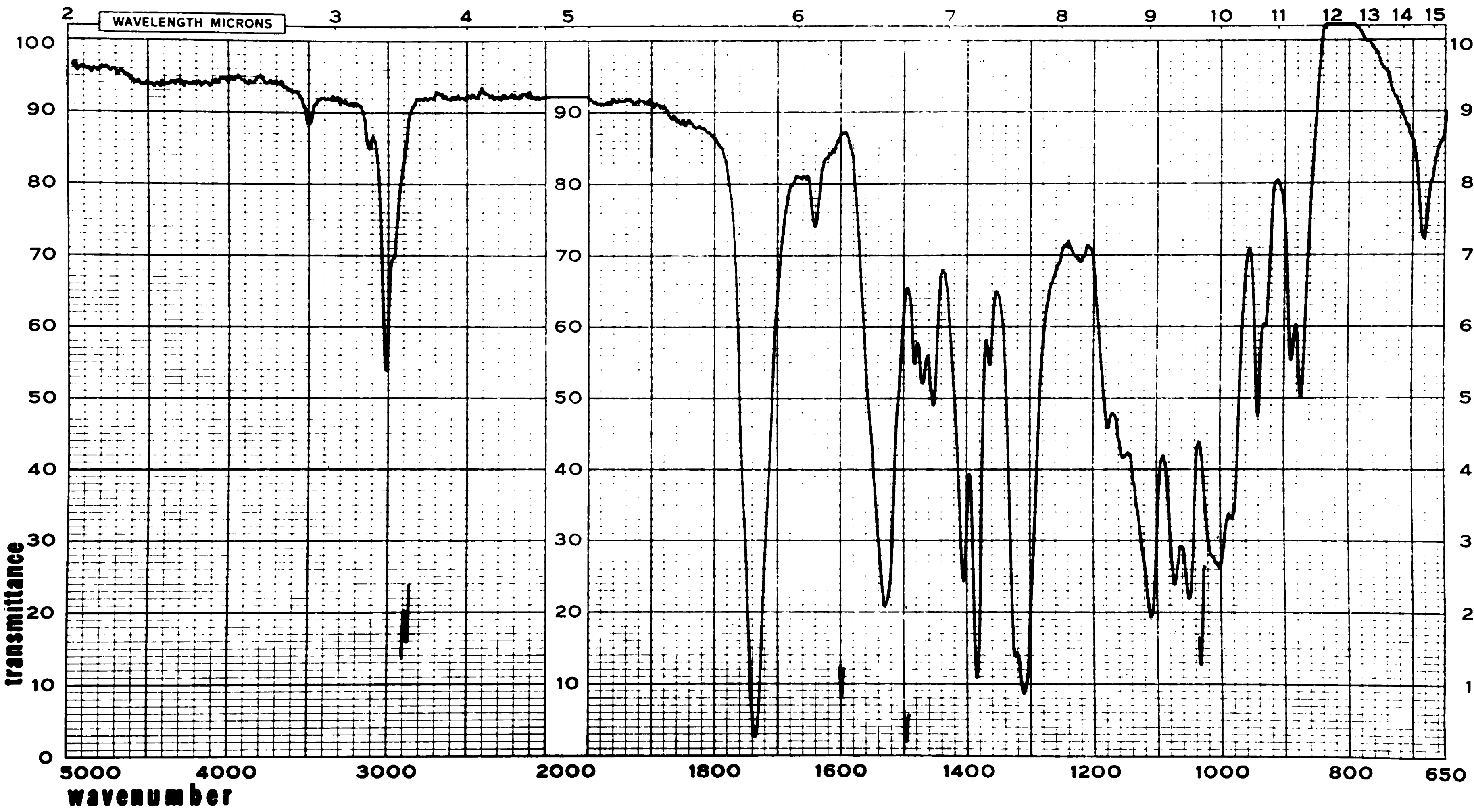


Figure 21. Infrared spectrum of ethyl trans-3-(m-nitrophenyl)-2-propenylnitrosocarbamate (CCl_4).

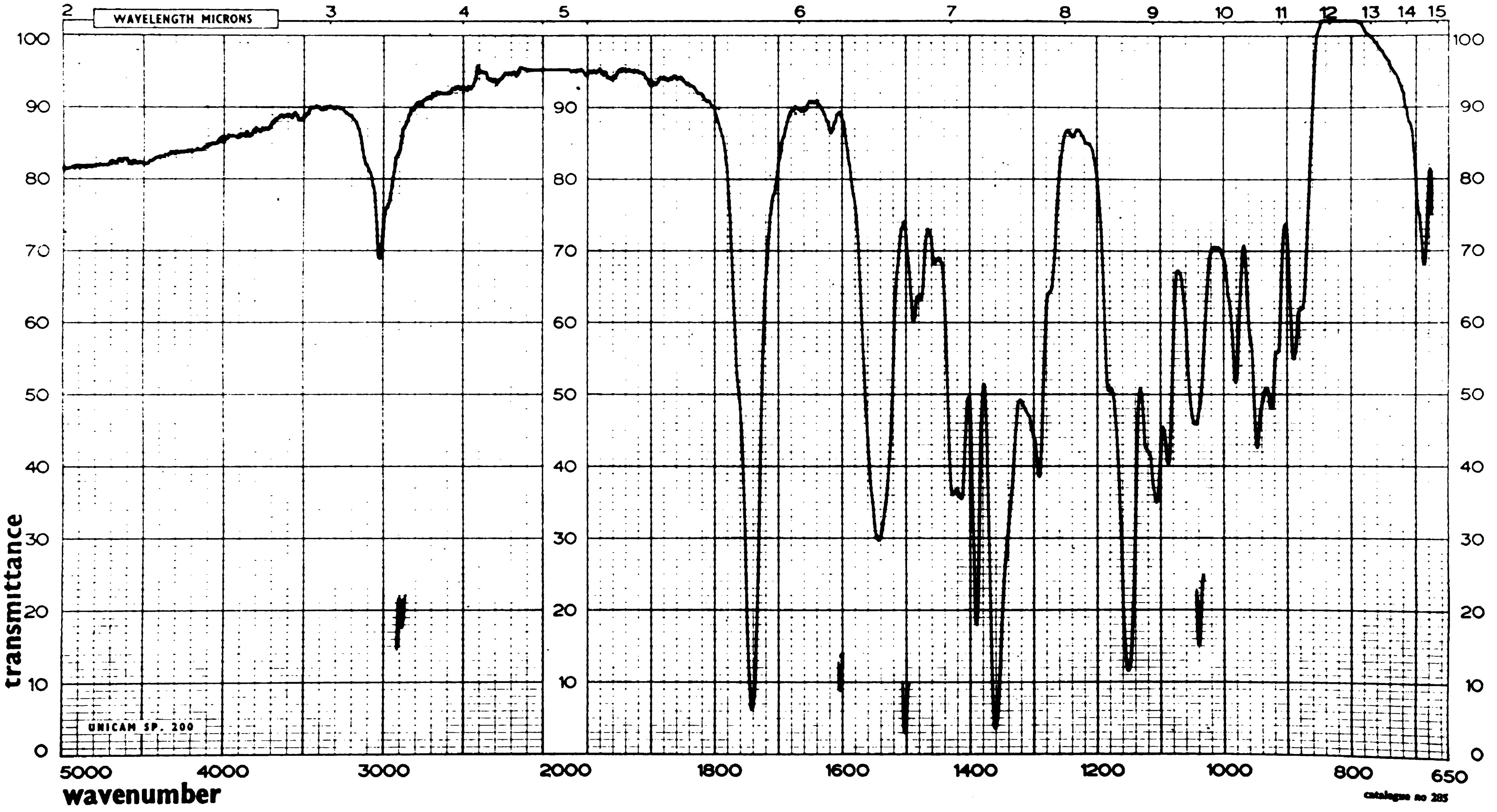


Figure 22. Infrared spectrum of ethyl trans-3-(p-chlorophenyl)-2-propenylnitrosocarbamate (CCl_4).

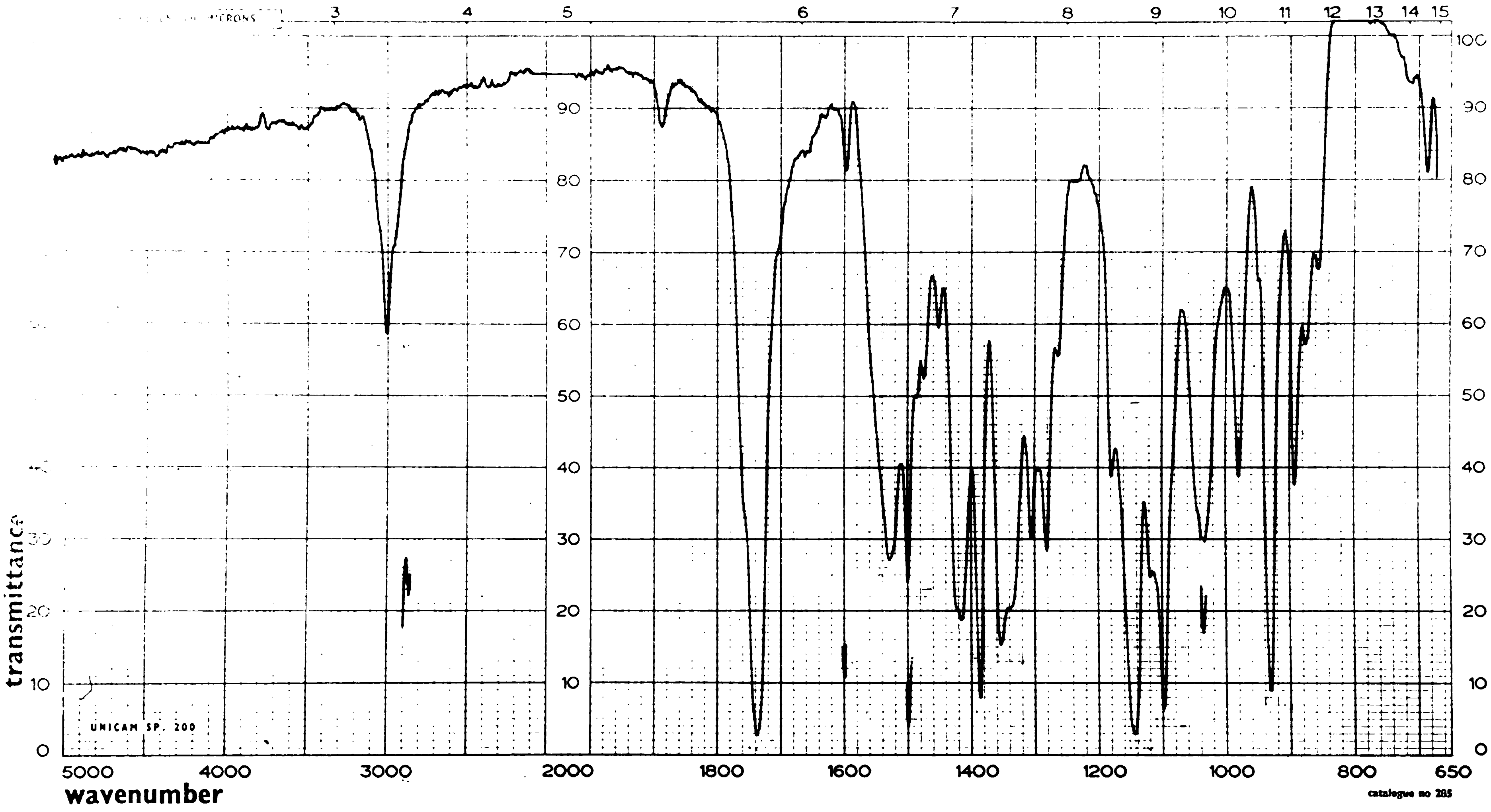


Figure 23. Infrared spectrum of ethyl <u>trans</u>-3-phenyl-2-propenylnitrosocarbamate (CCl_4).

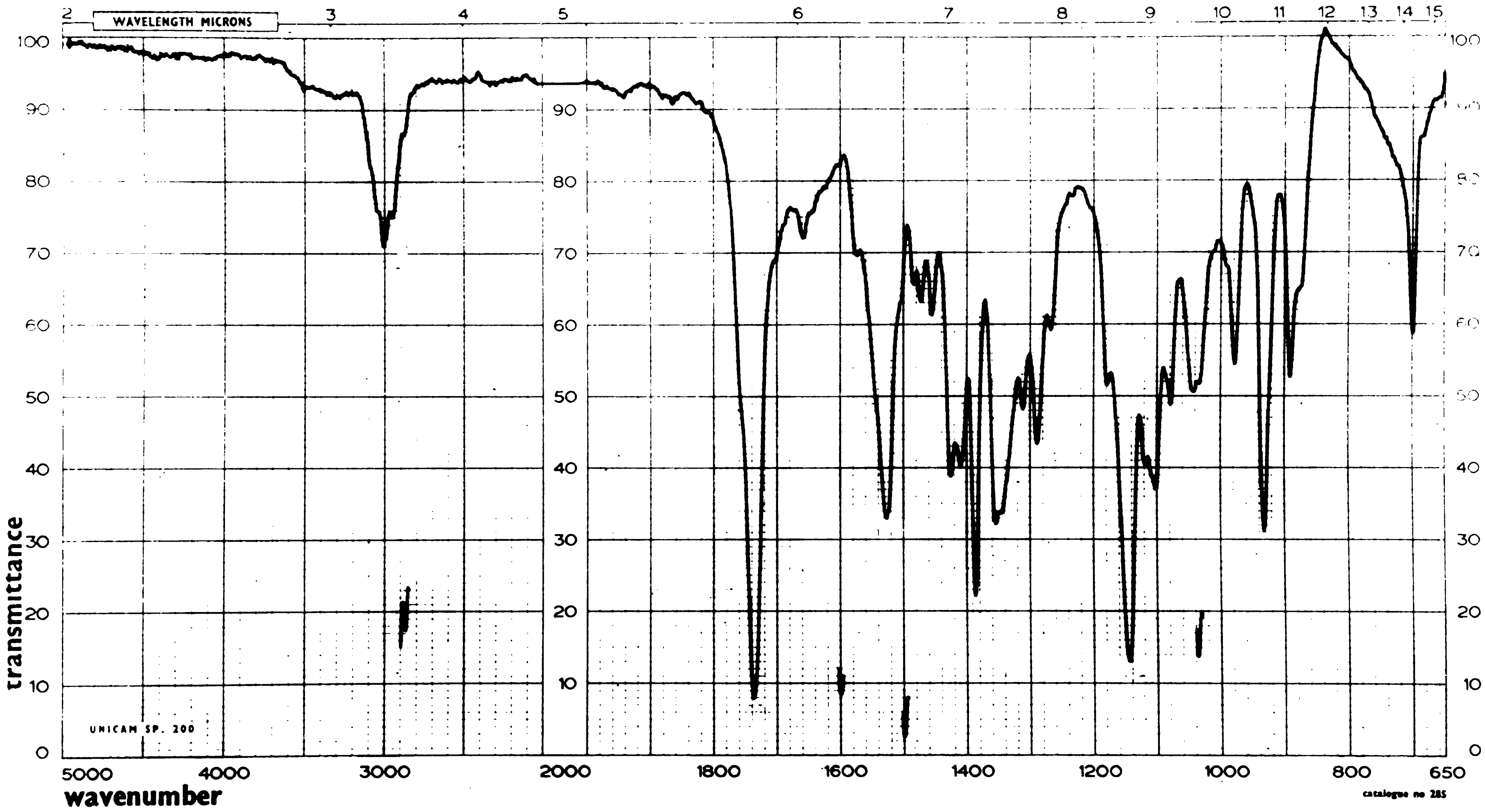


Figure 24. Infrared spectrum of ethyl <u>trans</u>-3-(<u>p</u>-tolyl)-2-propenylnitrosocarbamate (CCl_4).

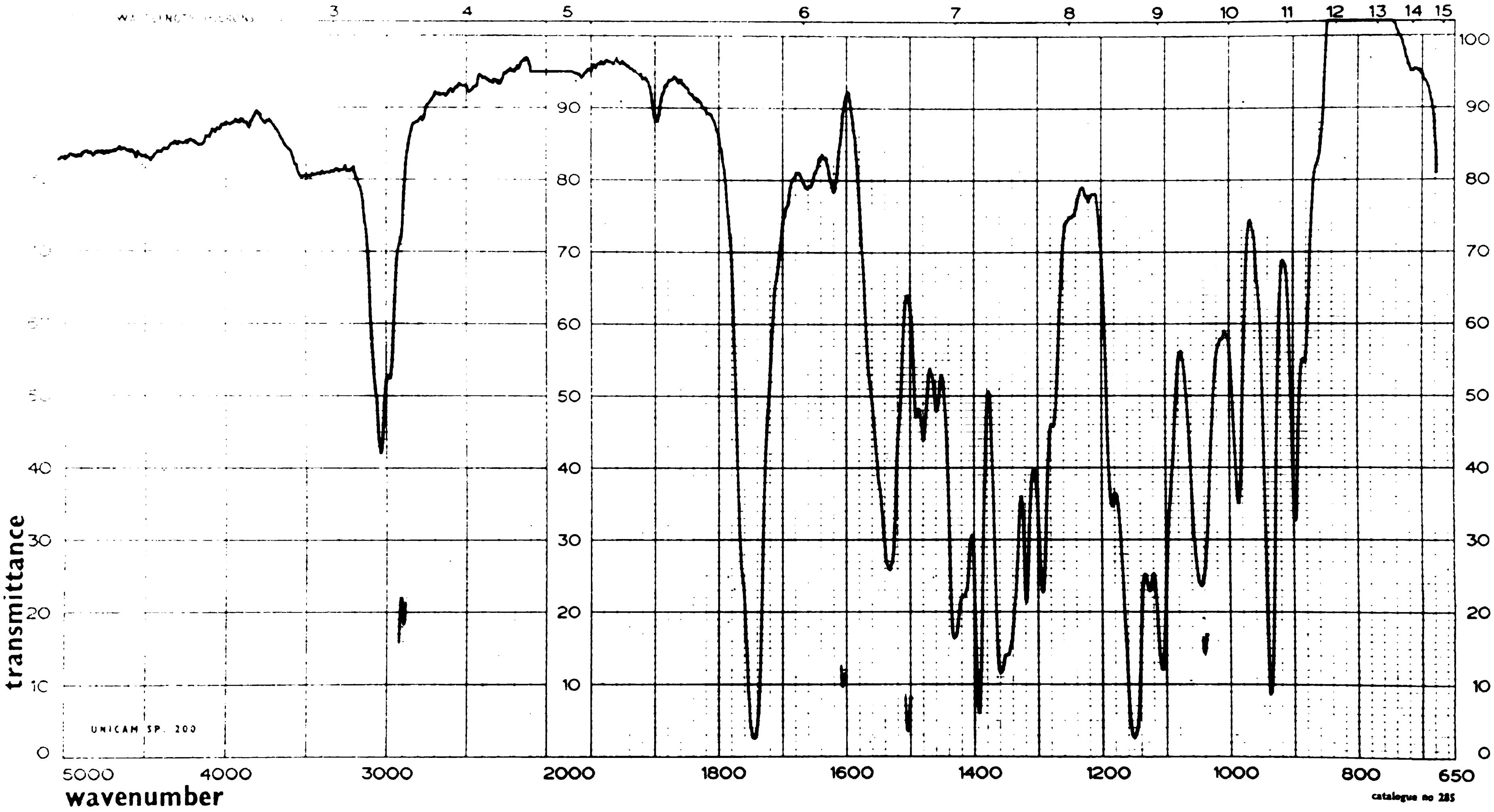


Figure 25. Infrared spectrum of pyrazole (KBr).

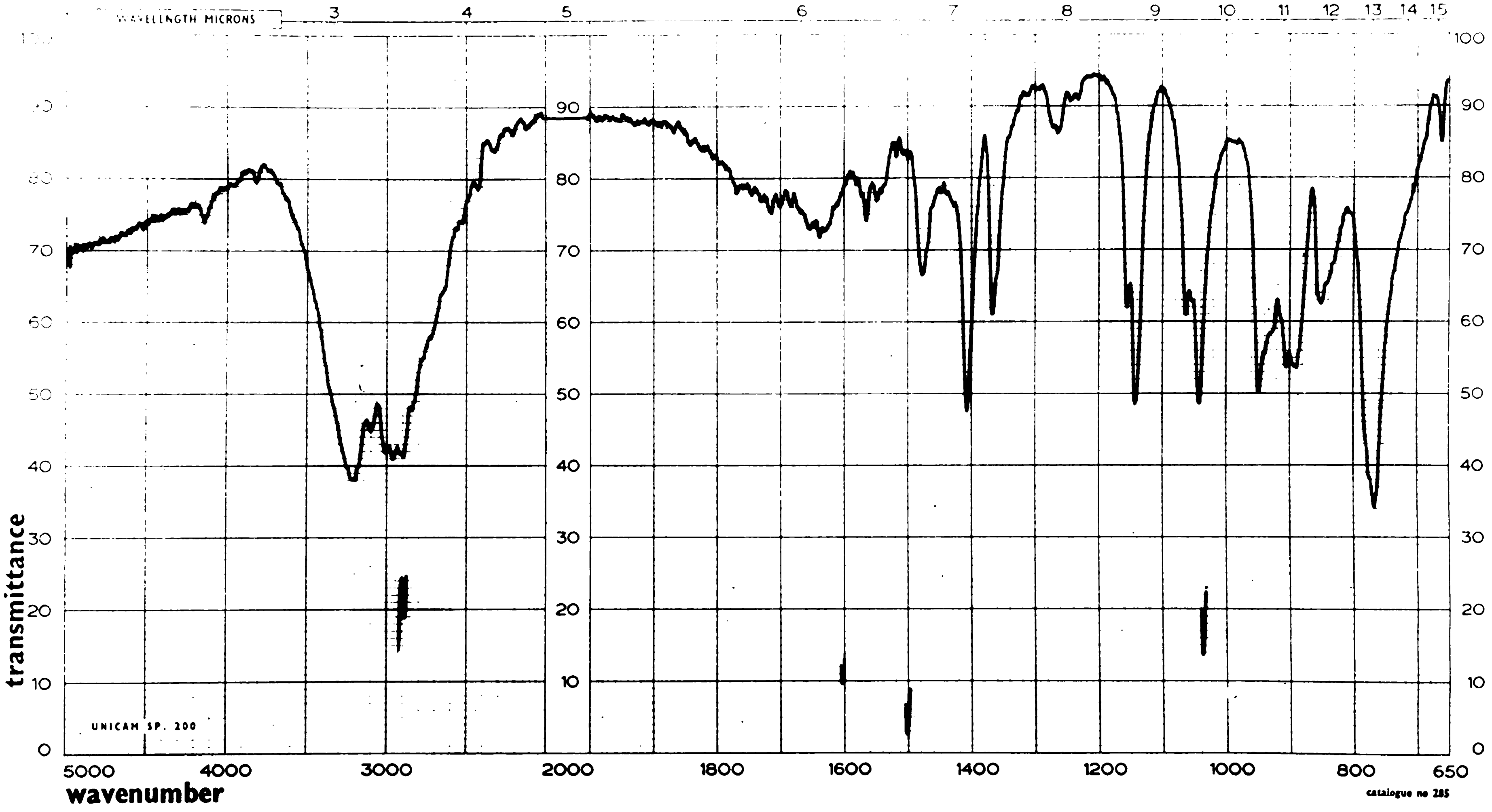


Figure 26. Infrared spectrum of 4-methylpyrazole (film).

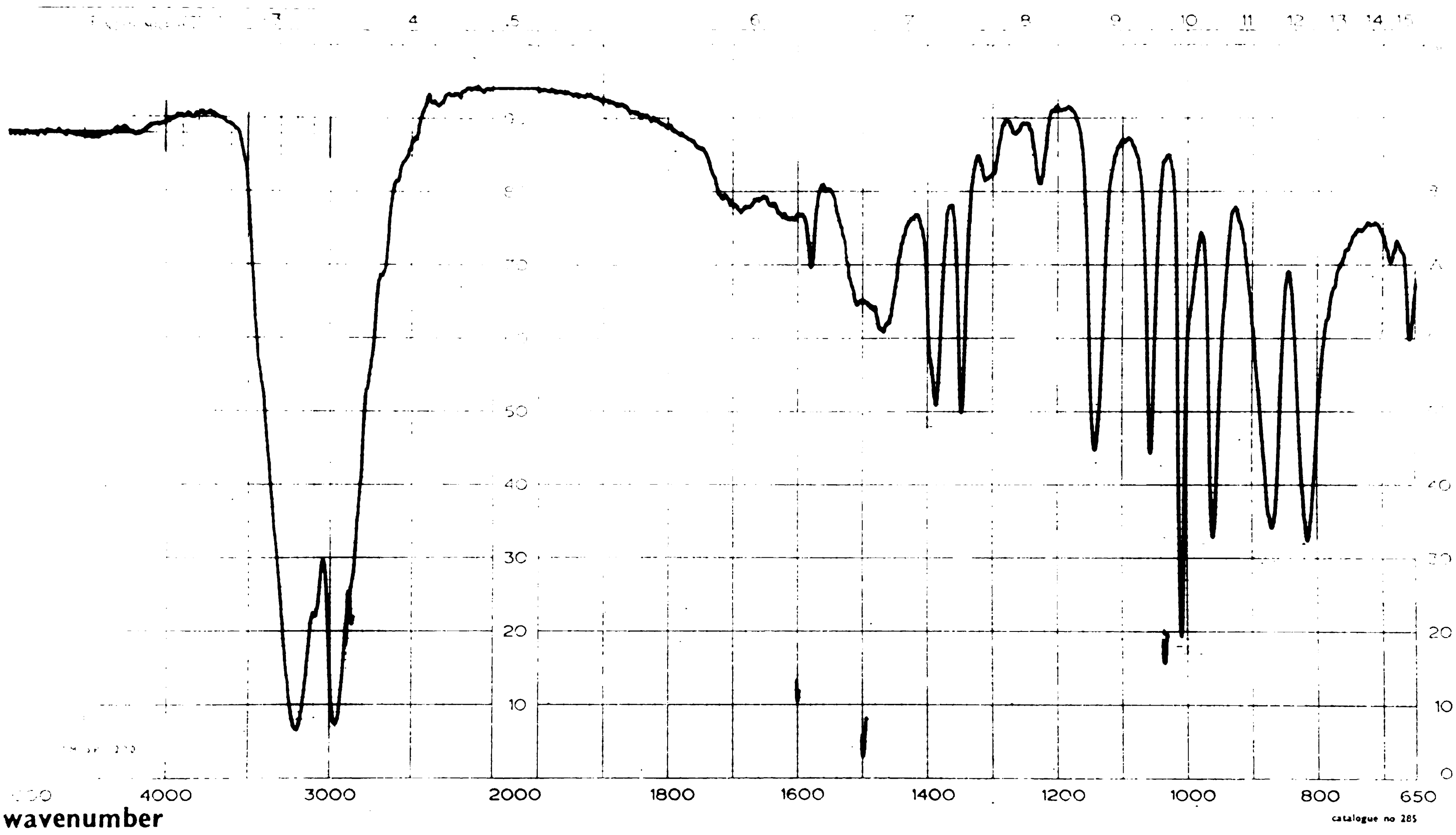


Figure 27. Infrared spectrum of 3(5)-methylpyrazole (film).

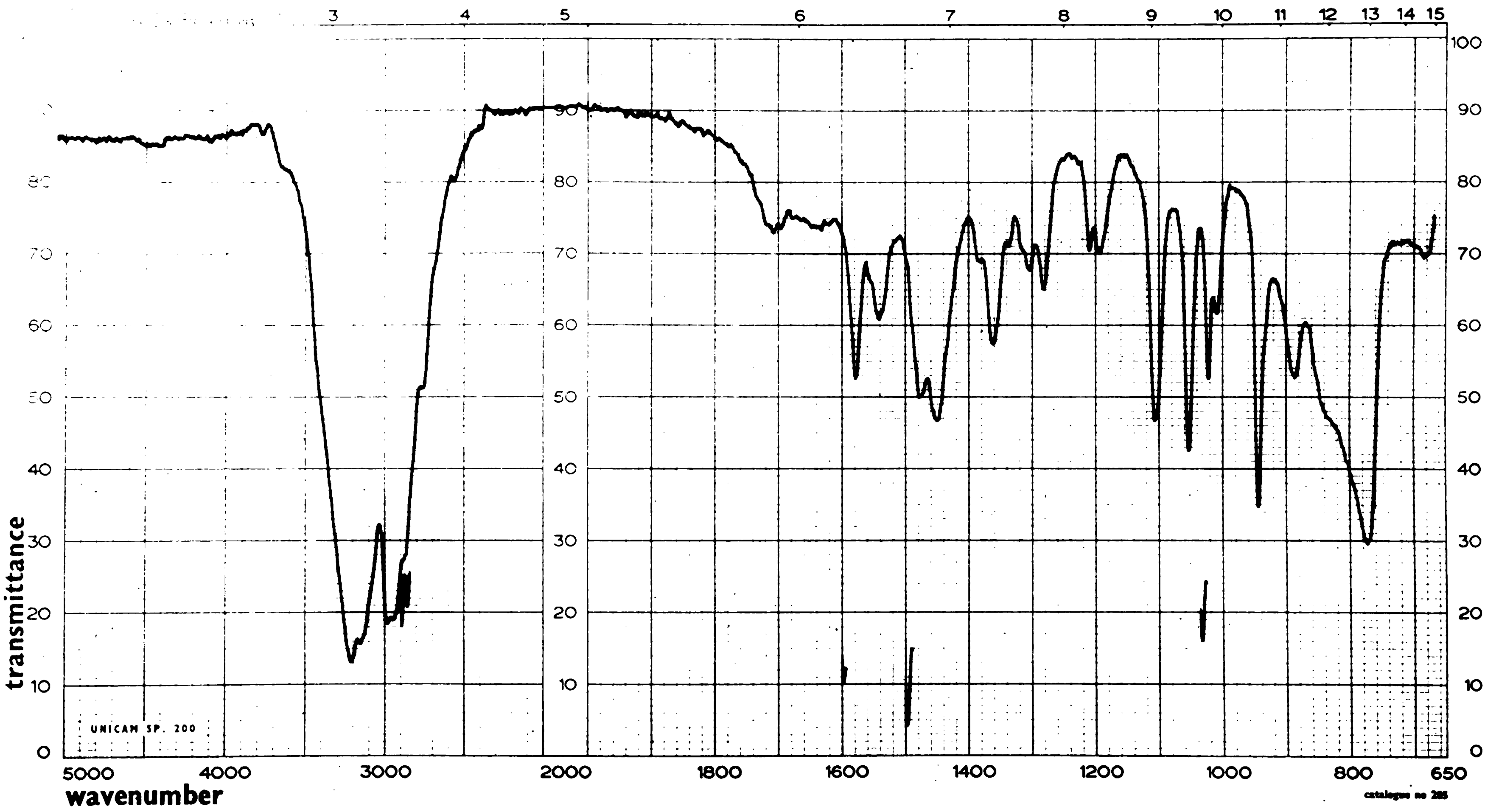
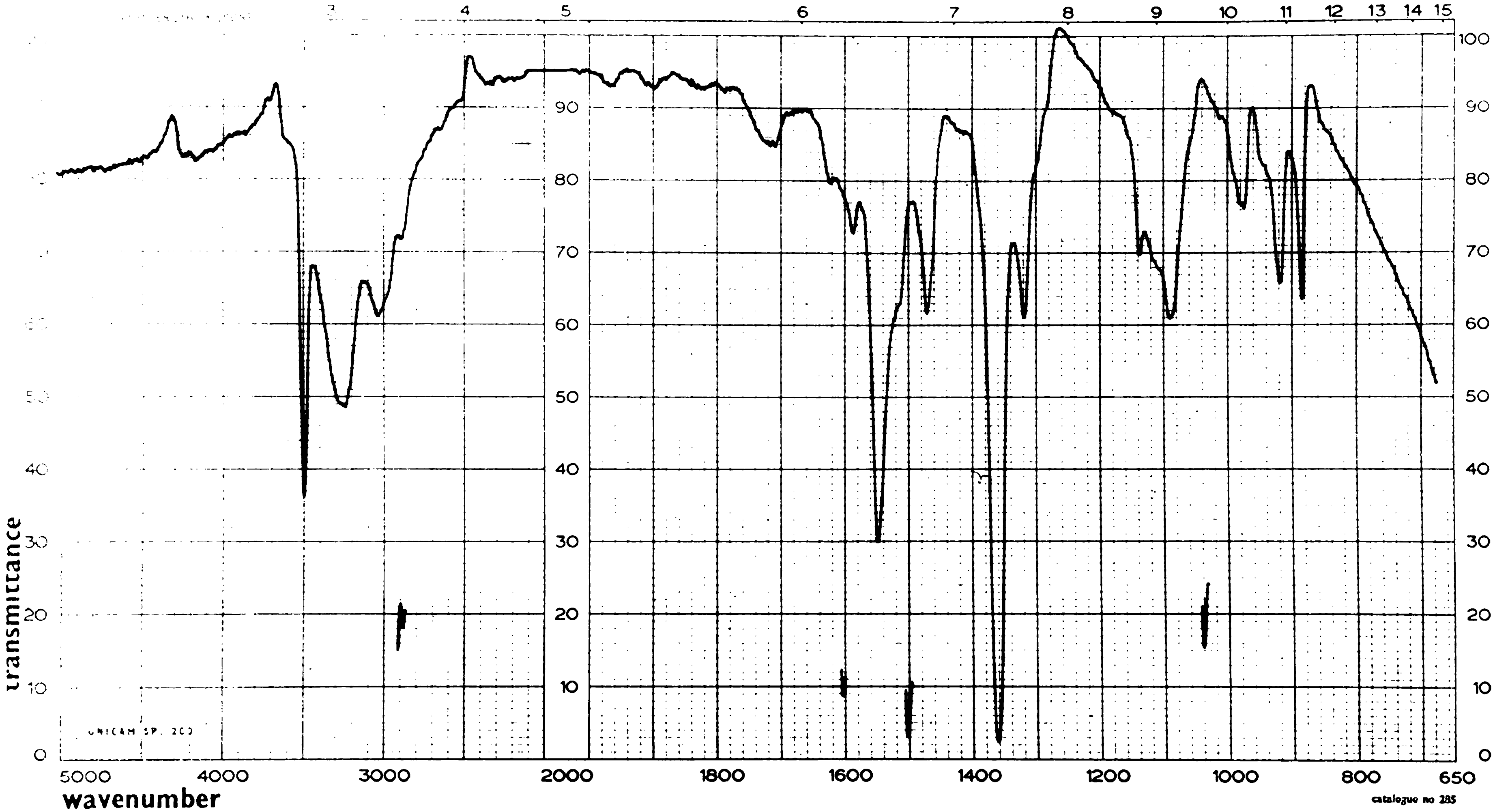


Figure 28. Infrared spectrum of 3(5)-(m-nitrophenyl)pyrazole ($HCCl_3$).



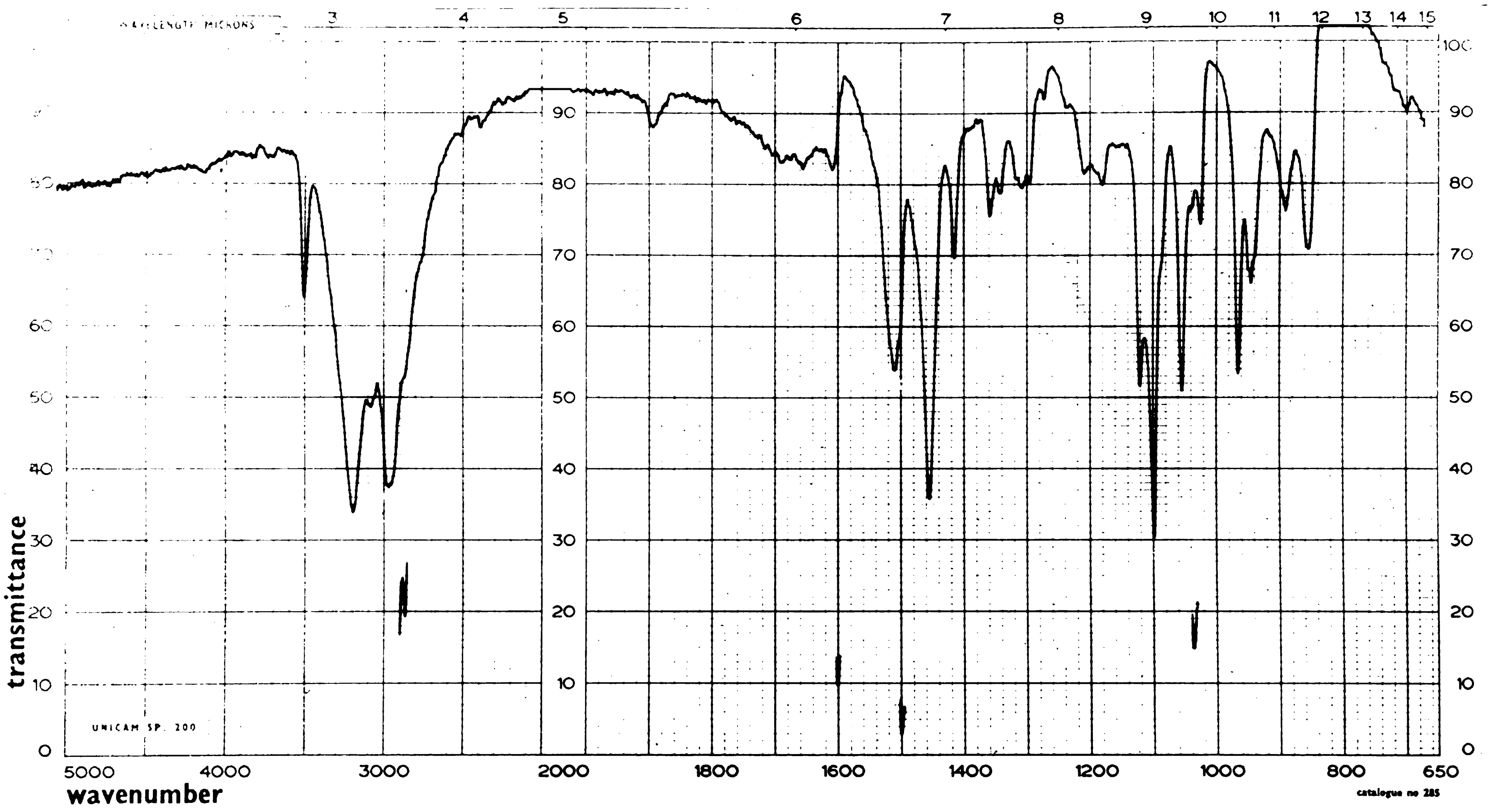


Figure 29. Infrared spectrum of 3(5)-(p-chlorophenyl)pyrazole (CCl_4).

Figure 30. Infrared spectrum of 3(5)-phenylpyrazole (CCl_4).

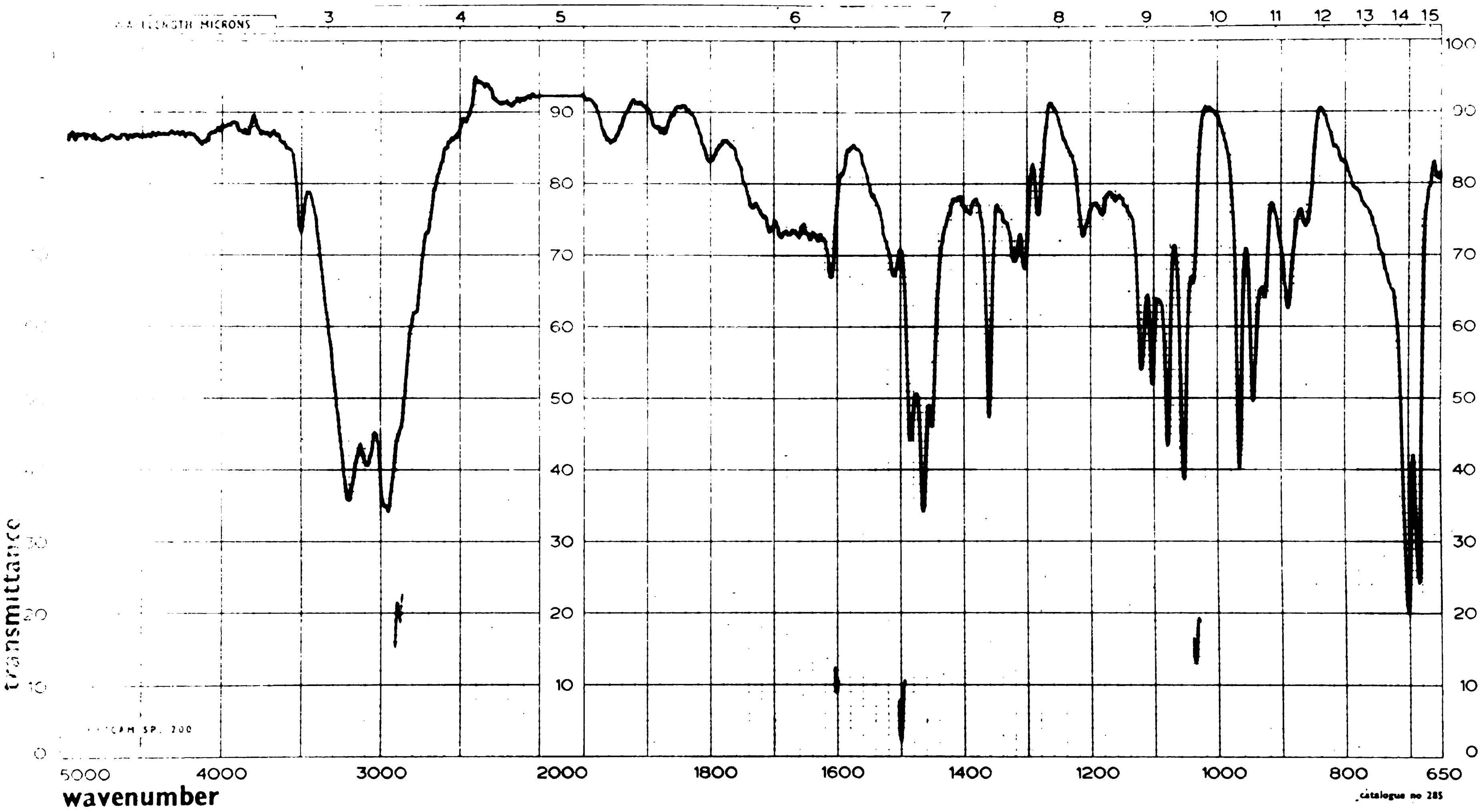


Figure 31. Infrared spectrum of 3(5)-(p-tolyl)pyrazole (CCl_4).

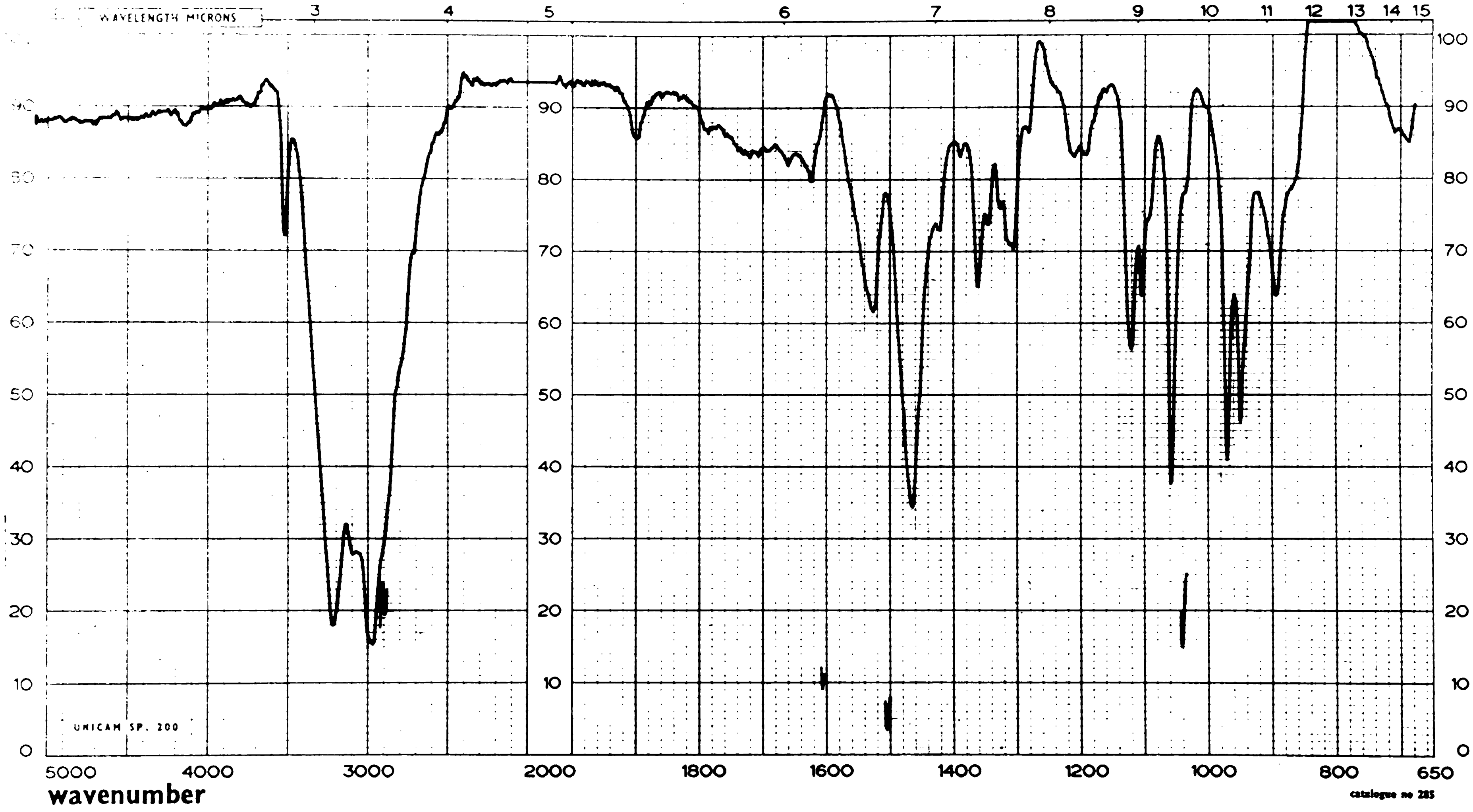
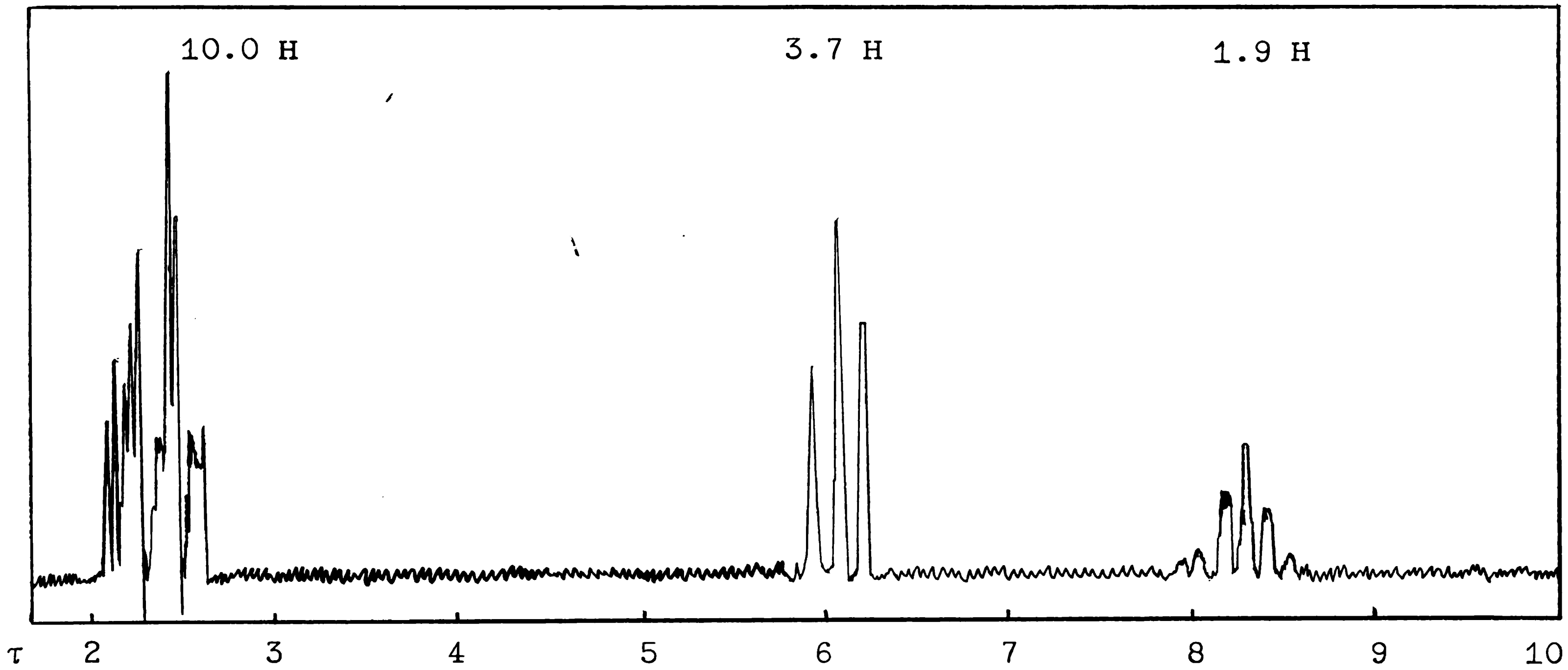
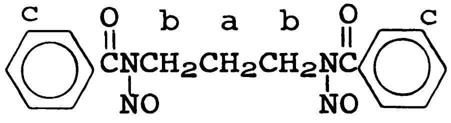


Figure 32. Nuclear magnetic resonance spectrum of N,N'-trimethylenebis-(N-nitrosobenzamide) ($DCCl_3$).



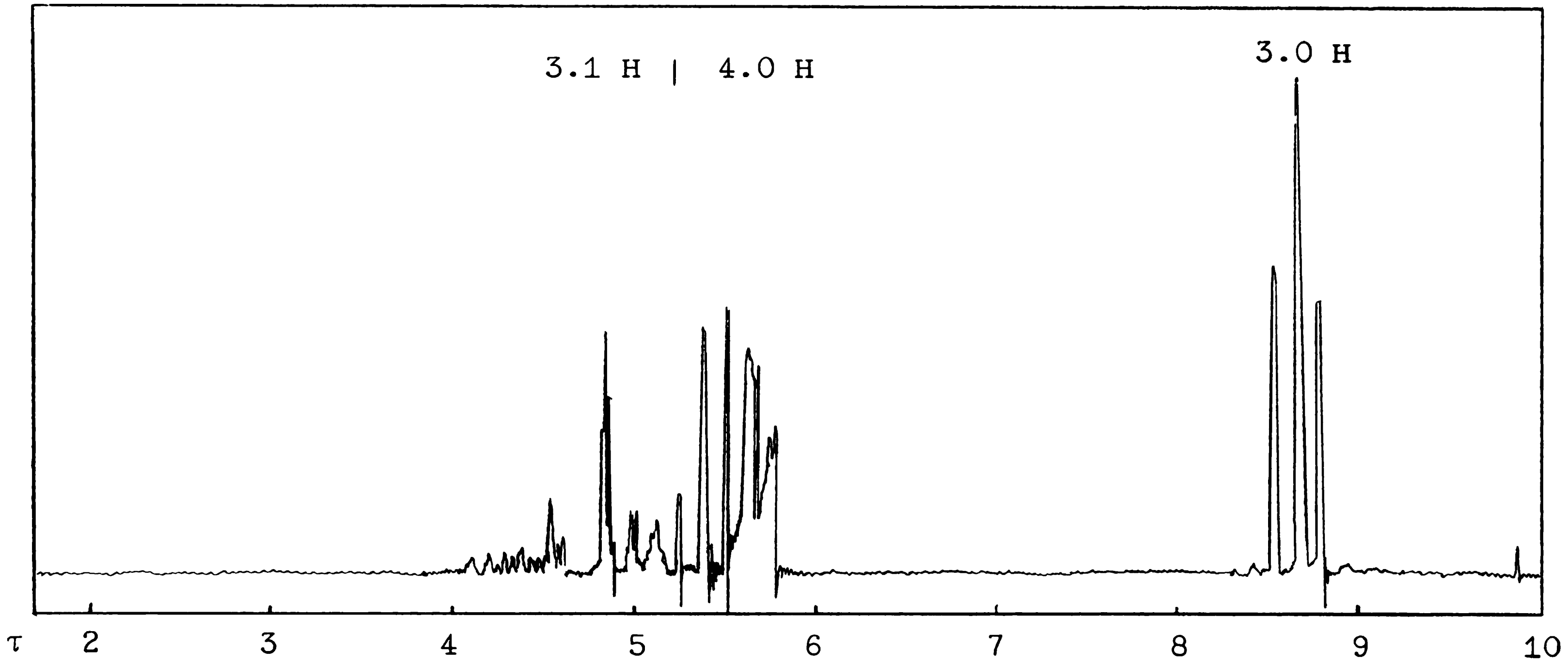


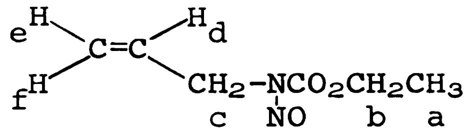
Assignments (τ)

a	8.32
b	6.06
c	2.61-2.24

J_{ab} = 7.1 cps

Figure 33. Nuclear magnetic resonance spectrum of ethyl allylnitrosocarbamate (neat).

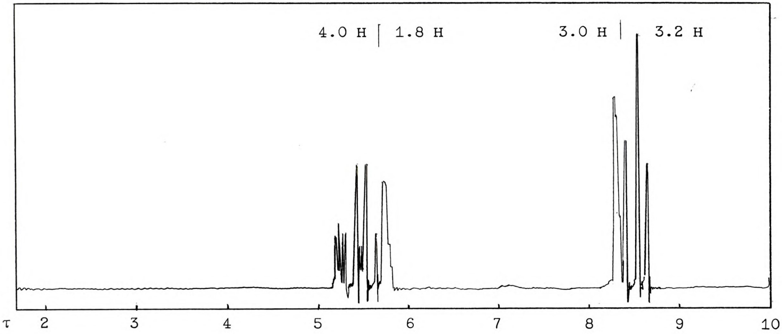


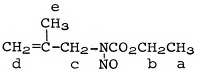


Assignments (τ)	
a	8.66
b	5.47
c	5.63
d,e,f	5.17-4.00

J_{ab} = 7 cps

Figure 34. Nuclear magnetic resonance spectrum of ethyl 2-methyl-2-propenylnitrosocarbamate (CCl_4).

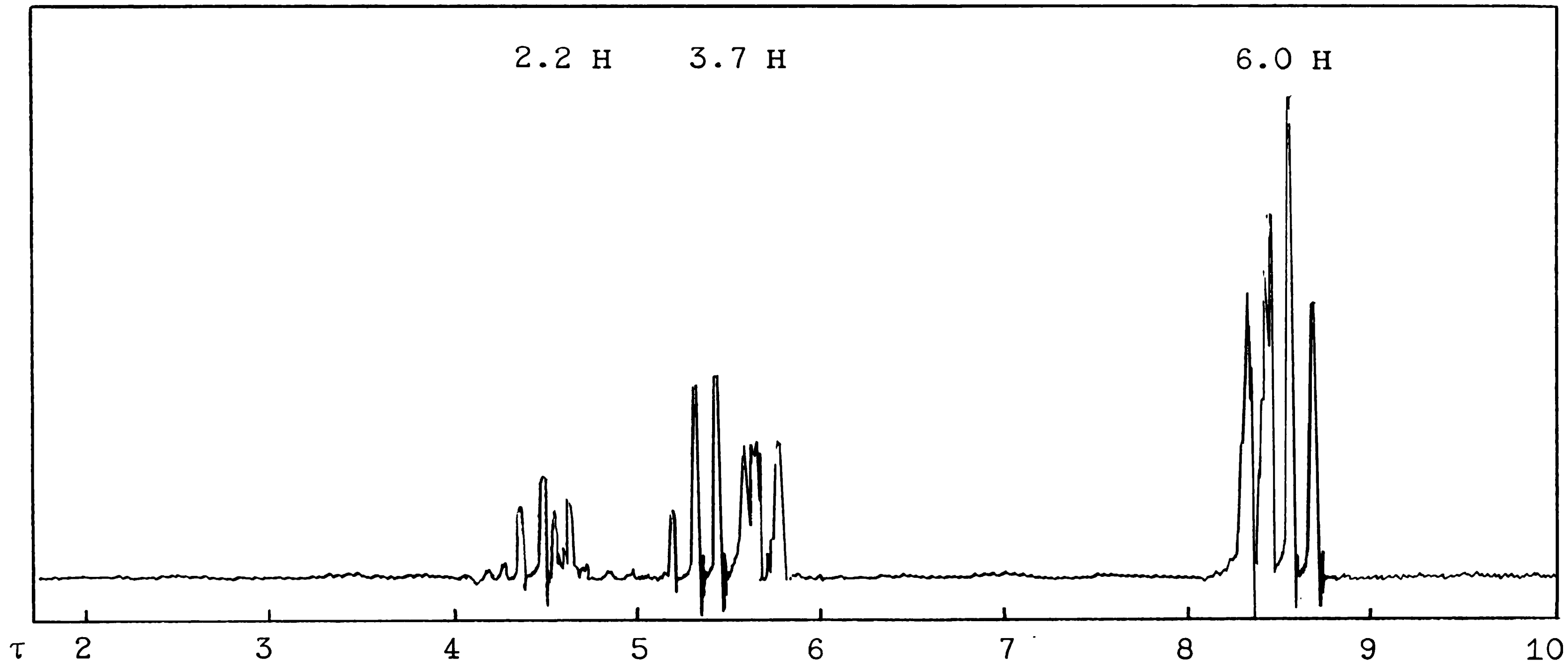


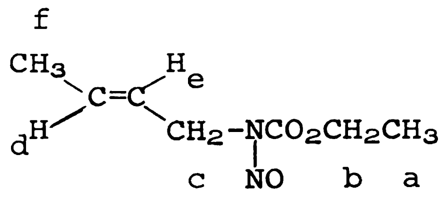

$\underset{d}{CH_2}=\overset{\overset{e}{CH_3}}{C}-\underset{c}{CH_2}-\underset{NO}{N}CO_2\underset{b}{CH_2}\underset{a}{CH_3}$

Assignments (τ)	
a	8.55
b	5.50
c	5.73
d	5.50, 5.24
e	8.35

J_{ab} = 7.0 cps

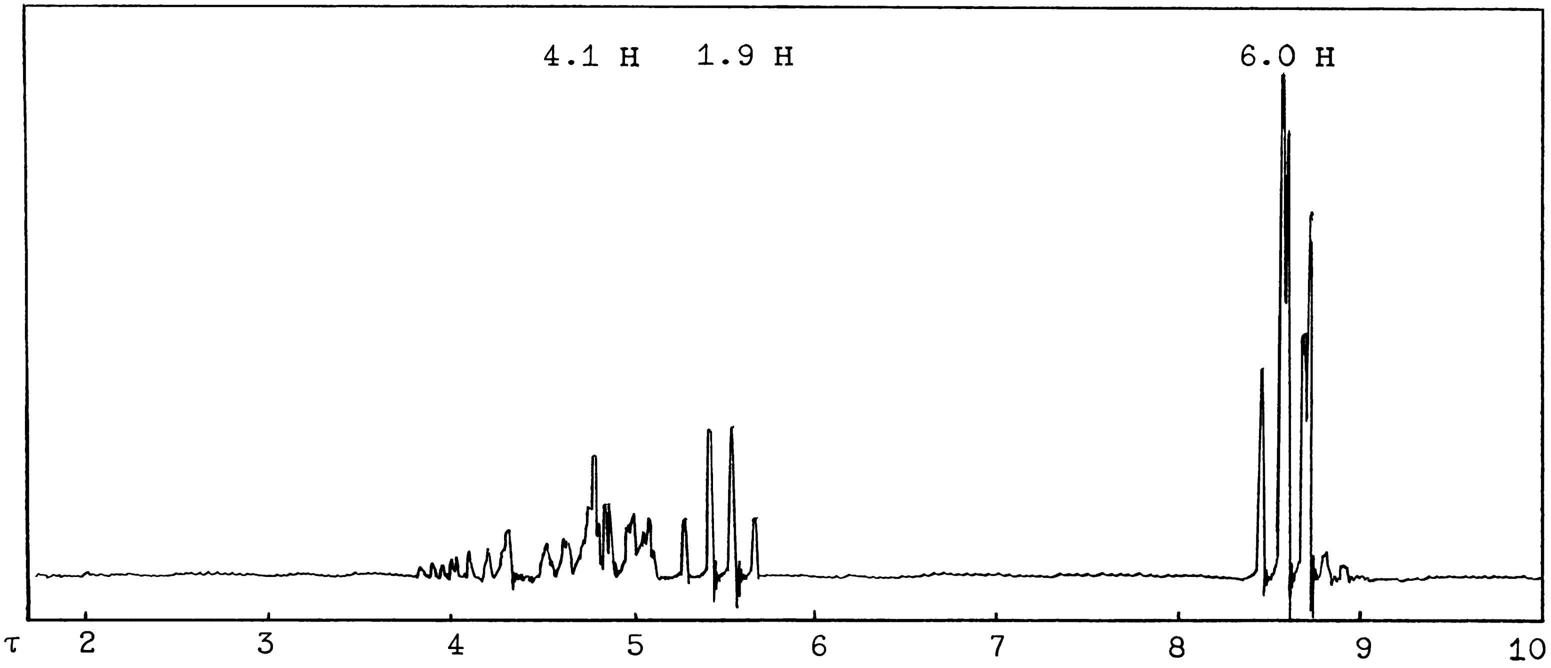
Figure 35. Nuclear magnetic resonance spectrum of ethyl <u>trans</u>-2-butenylnitrosocarbamate (neat).

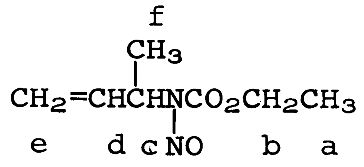




Assignments (τ)			
a	8.57	J_{ab}	7.0 cps
b	5.45	J_{ce}	6 cps
c	5.70	J_{df}	6 cps
d,e	5.0-4.0		
f	8.38		

Figure 36. Nuclear magnetic resonance spectrum of ethyl 1-methyl-2-propenylnitrosocarbamate (neat).





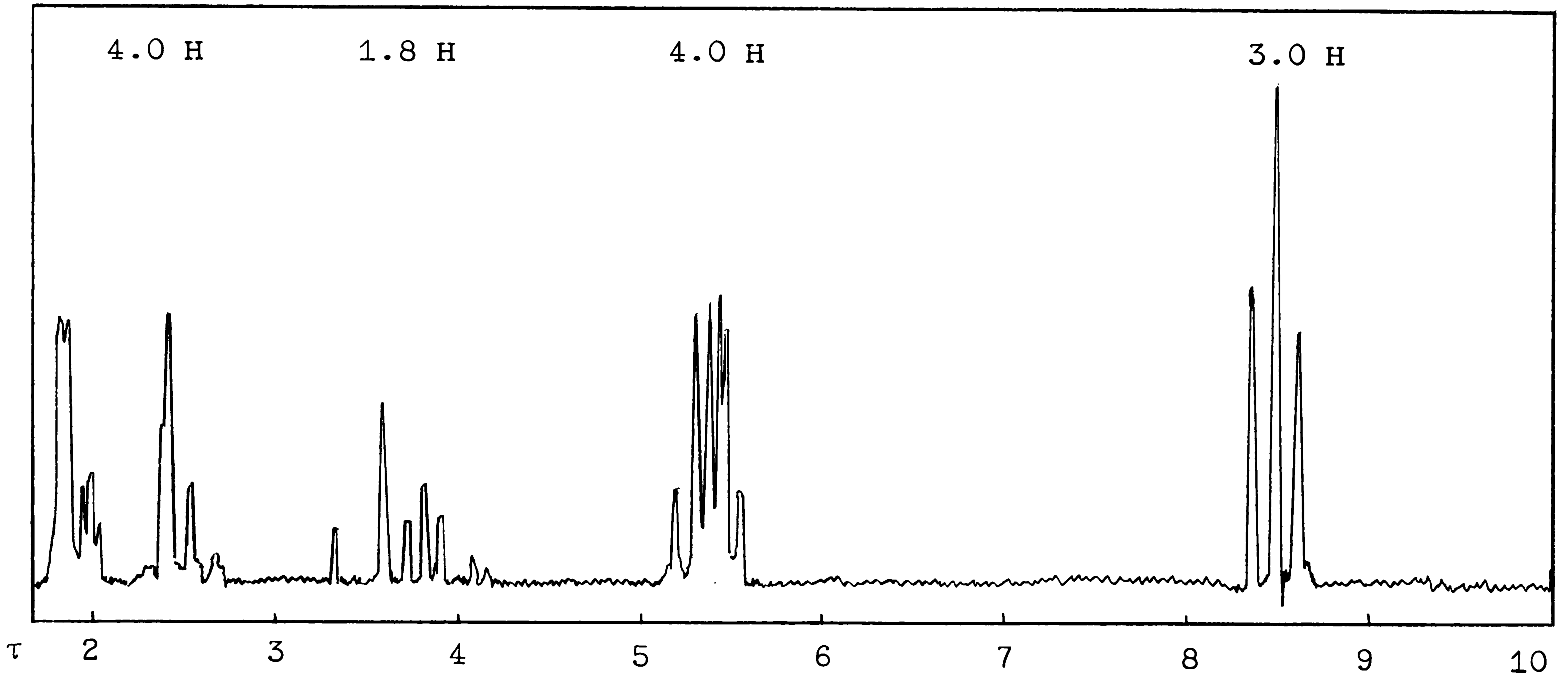
$$\underset{e}{CH_2}=\underset{d}{CH}\overset{\overset{f}{CH_3}}{\underset{c}{C}H}\underset{NO}{N}CO_2\underset{b}{CH_2}\underset{a}{CH_3}$$

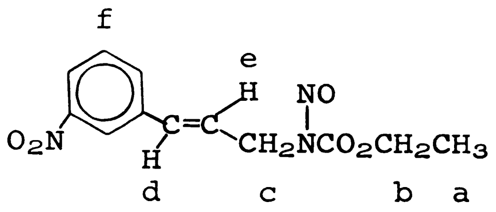
Assignments (τ)	
a	8.58
b	5.50
c,d,e	5.15-4.02
f	8.70

J_{ab} = 7.0 cps

J_{cf} = 7 cps

Figure 37. Nuclear magnetic resonance spectrum of ethyl trans-3-(m-nitrophenyl)-2-propenylnitrosocarbamate ($DCCl_3$).

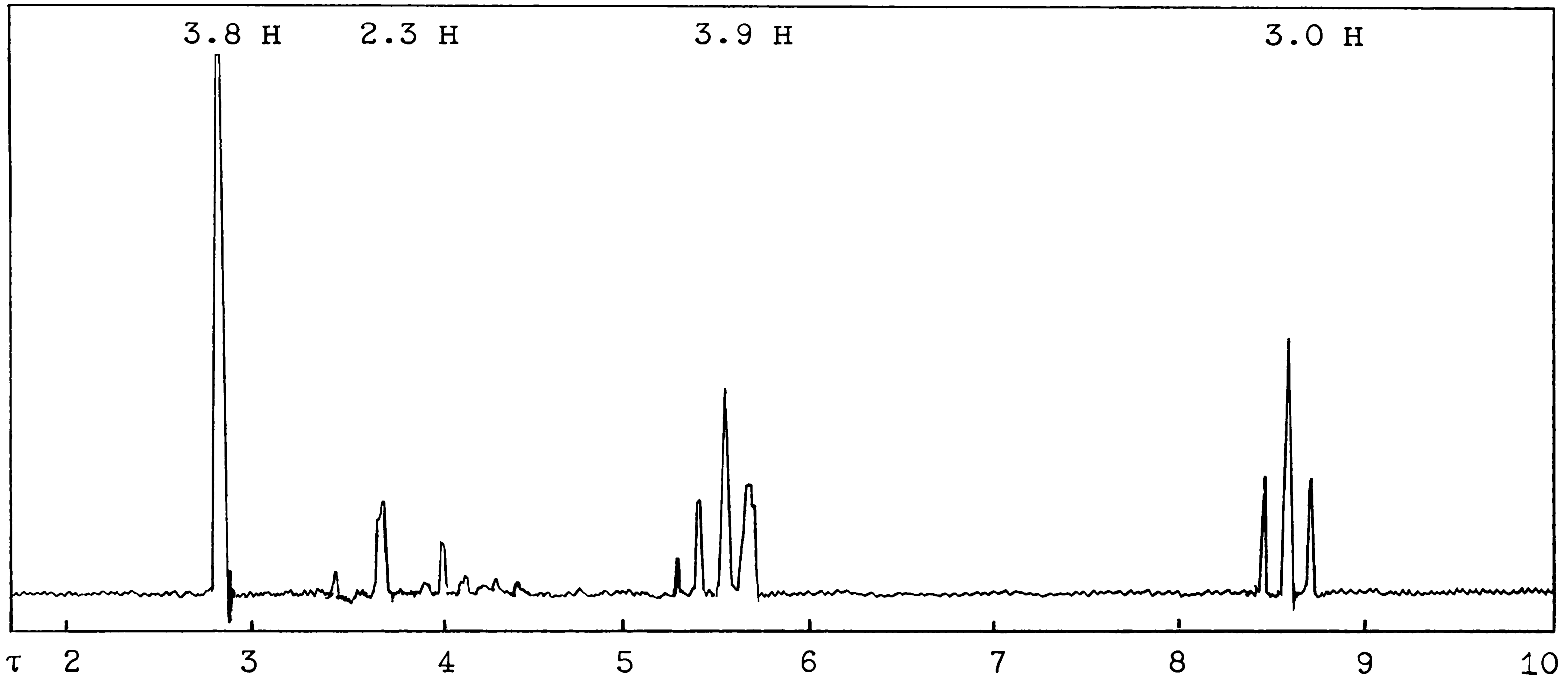


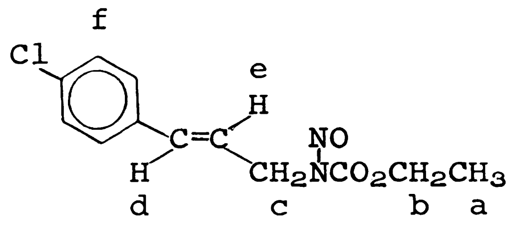


Assignments (τ)	
a	8.52
b	5.44
c	5.47
d	4.17-3.70
e	3.57-3.30
f	2.71-1.80

J_{ab} = 7.2 cps
J_{ce} = 5.5 cps
J_{de} = 15.8 cps

Figure 38. Nuclear magnetic resonance spectrum of ethyl *trans*-3-(*p*-chlorophenyl)-2-propenylnitrosocarbamate (CCl_4).

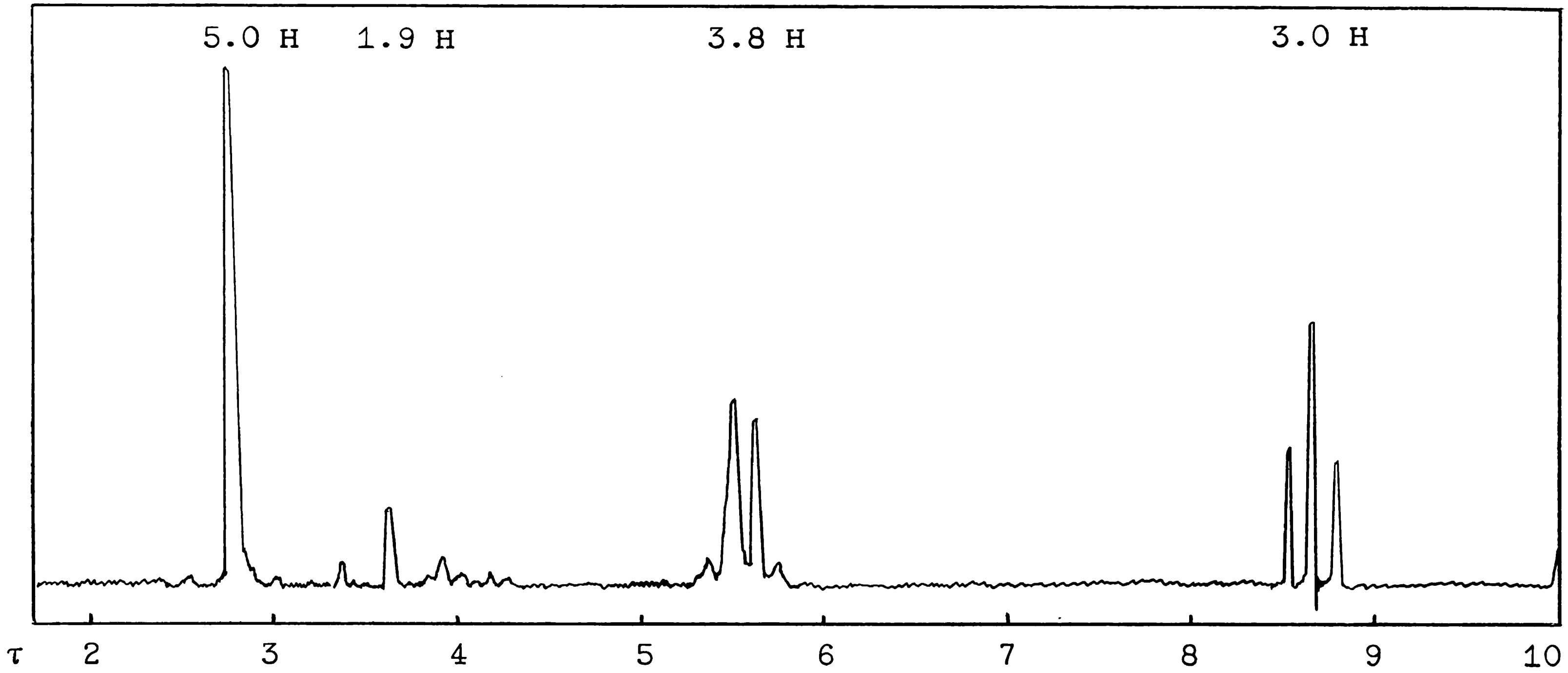


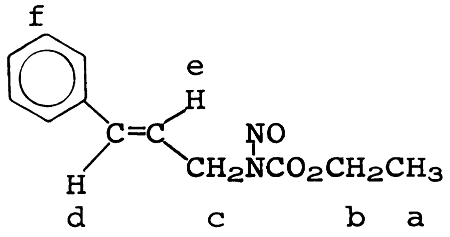


Assignments (τ)	
a	8.57
b	5.52
c	5.63
d	3.70-3.44
e	4.44-3.97
f	2.84

J_{ab} = 7.3 cps
J_{ce} = 5.9 cps
J_{de} = 15.6 cps

Figure 39. Nuclear magnetic resonance spectrum of ethyl <u>trans</u>-3-phenyl-2-propenylnitrosocarbamate (neat).

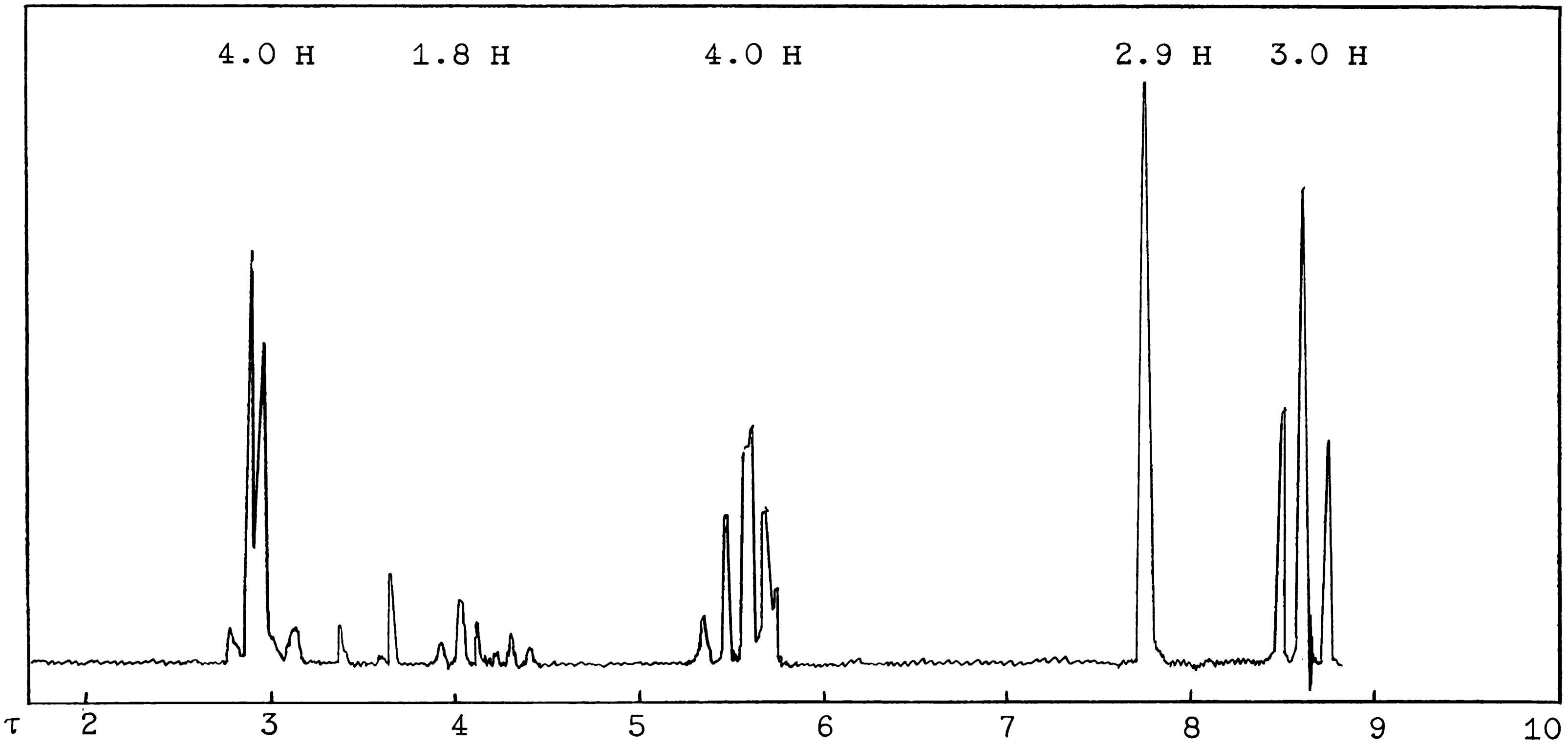


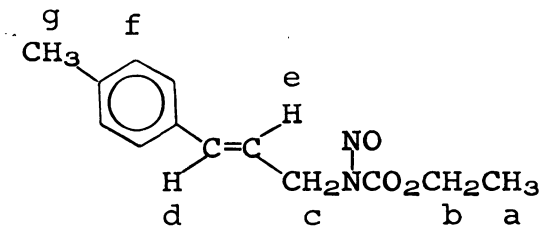


Assignments (τ)	
a	8.68
b	5.57
c	5.57
d	3.63-3.35
e	4.30-3.85
f	2.80

J_{ab} = 7.2 cps
J_{ce} = 5.6 cps
J_{de} = 15.8 cps

Figure 40. Nuclear magnetic resonance spectrum of ethyl *trans*-3-(*p*-tolyl)-2-propenylnitrosocarbamate (CCl_4).

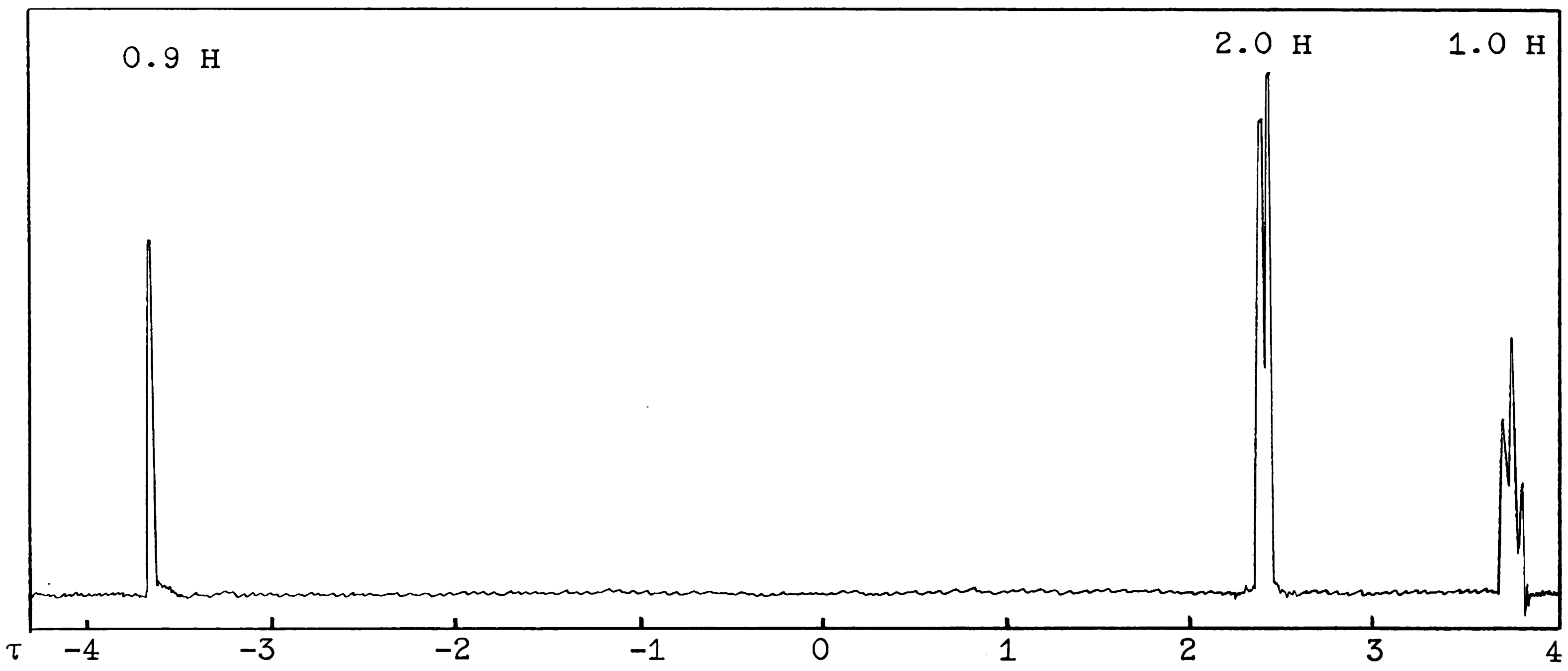


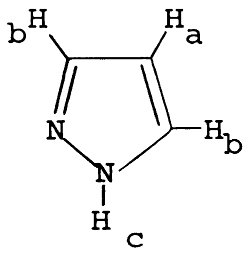


Assignments (τ)	
a	8.62
b	5.55
c	5.65
d	3.70-3.39
e	4.47-3.98
f	2.95
g	7.75

J_{ab} = 7.1 cps
J_{ce} = 6.1 cps
J_{de} = 15.8 cps

Figure 41. Nuclear magnetic resonance spectrum of pyrazole (CCl_4).

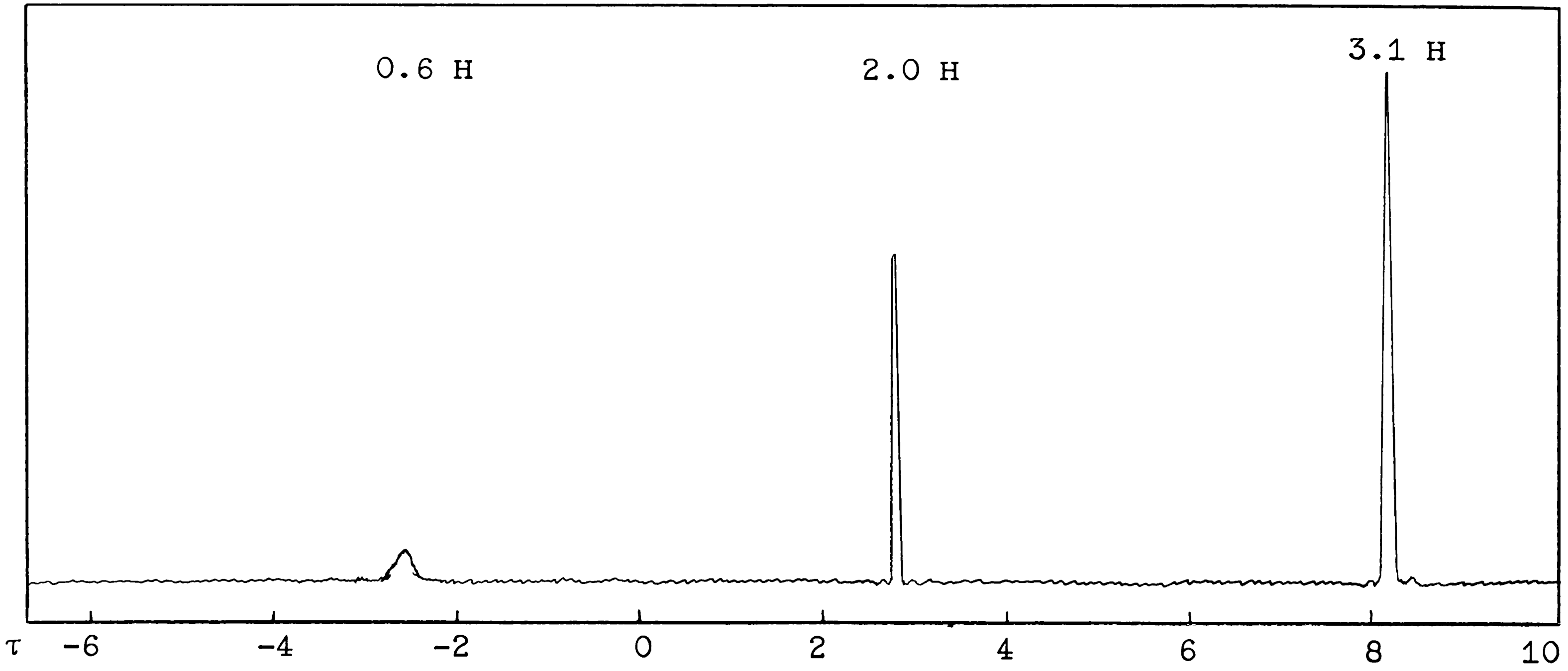


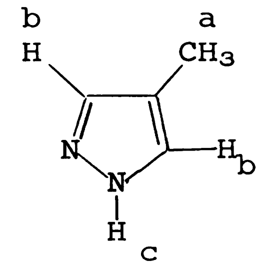


Assignments (τ)	
a	3.73
b	2.40
c	-3.65

$J_{ab} = 2.0$ cps

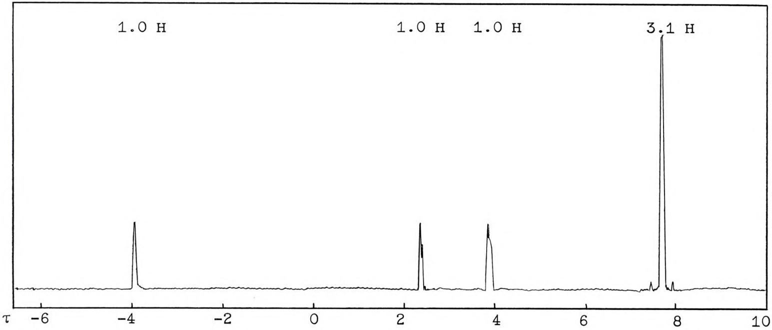
Figure 42. Nuclear magnetic resonance spectrum of 4-methylpyrazole (CCl_4).

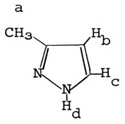




Assignments (τ)	
a	8.02
b	2.79
c	-2.65

Figure 43. Nuclear magnetic resonance spectrum of 3(5)-methylpyrazole (neat).

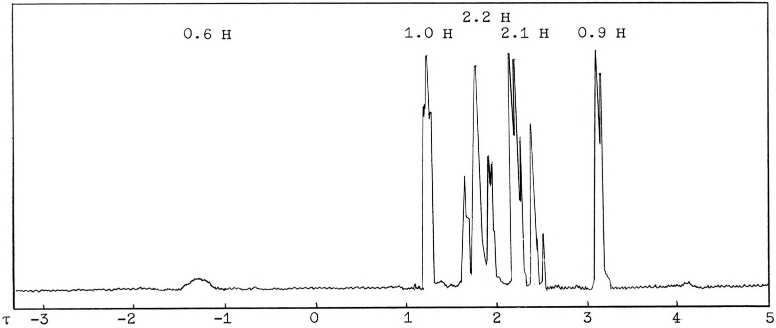


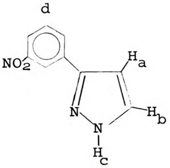


Assignments (τ)	
a	7.75
b	3.89
c	2.35
d	-3.90

J_{bc} = 1.7 cps

Figure 44. Nuclear magnetic resonance spectrum of 3(5)-(m-nitrophenyl)pyrazole (acetone).

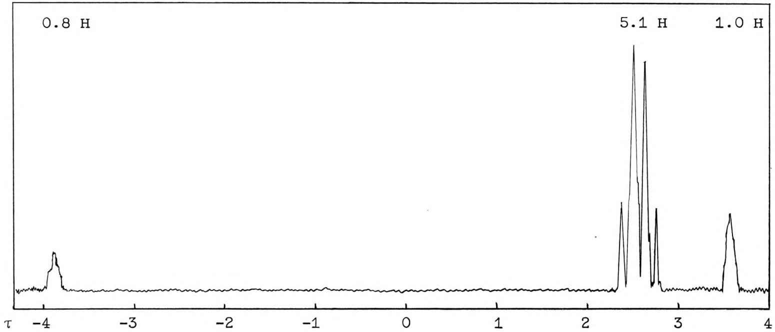


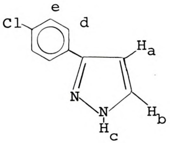


Assignments (τ)	
a	3.15
b	2.16
c	-1.30
d	2.56-1.20

$J_{ab} = 2.5$ cps

Figure 45. Nuclear magnetic resonance spectrum of 3(5)-(p-chlorophenyl)pyrazole (CCl_4).

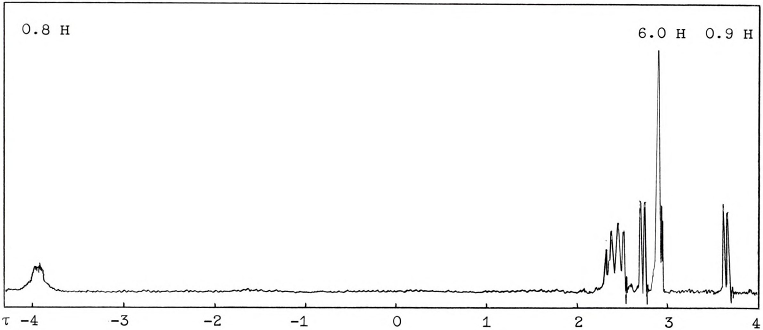


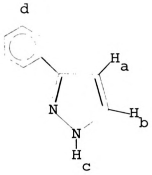


Assignments (τ)	
a	3.59
b	2.54
c	-3.88
d,e	2.73-2.24

J_{de} = 8.8 cps

Figure 46. Nuclear magnetic resonance spectrum of 3(5)-phenylpyrazole (CCl_4).

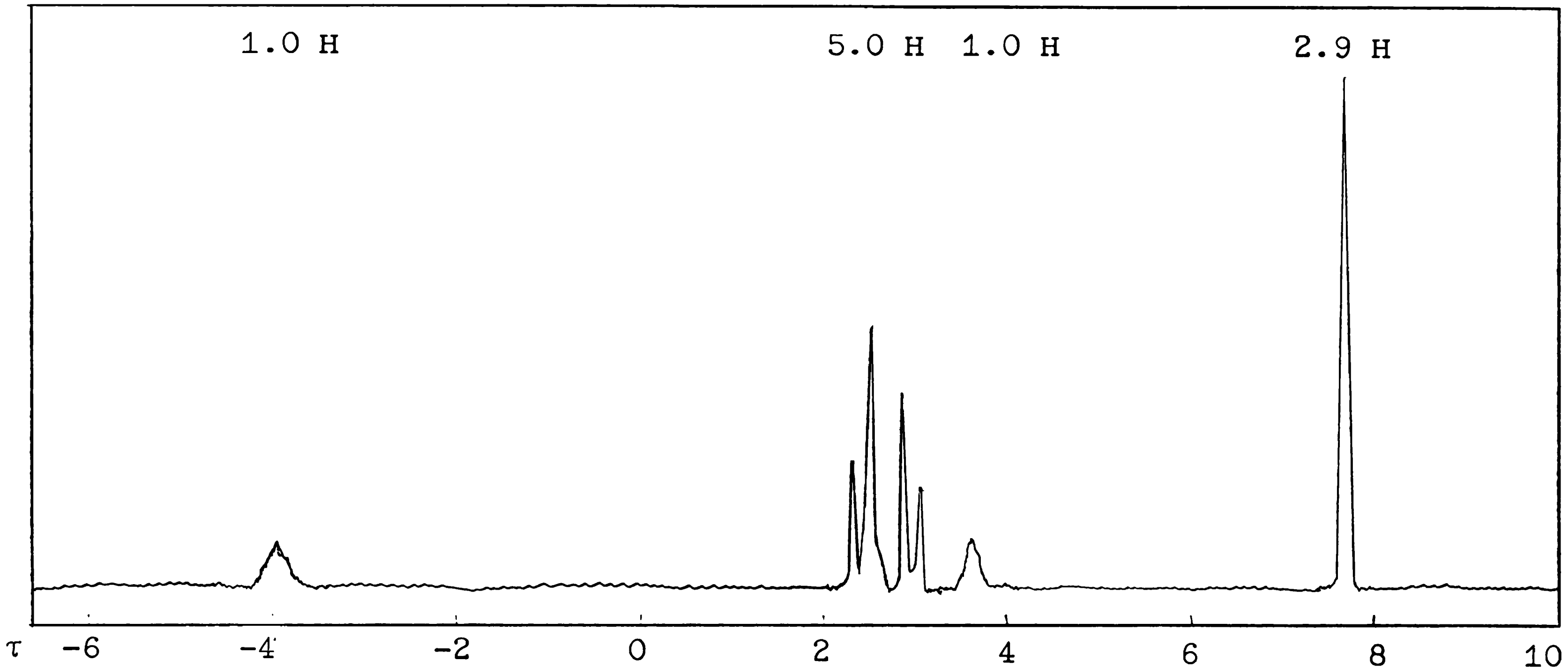


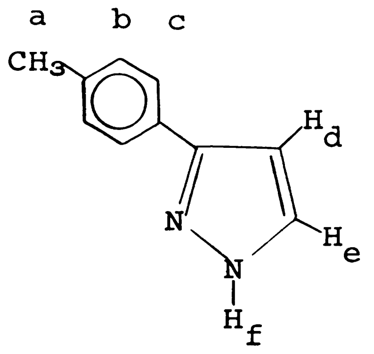


Assignments (τ)	
a	3.59
b	2.61
c	-4.02
d	2.92-2.25

$J_{ab} = 1.0$ cps

Figure 47. Nuclear magnetic resonance spectrum of 3(5)-(p-tolyl)pyrazole (CCl_4).





Assignments (τ)

a	7.74
b,c	3.11-2.34
d	3.62
e	2.50
f	-3.92

J_{bc} = 8.1 cps

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