# ARENESULFONYL- AND ARENESULFENYLPYRROLES

BY

NABEEL F. HAIDAR

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# ACKNOWLEDGMENT

The author wishes to express his gratitude to Professor E. Paul Papadopoulos who suggested this problem for investigation and directed the work.

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I dedicate this work to my parents:

FUAD AND YOLLANDA

# ABSTRACT

1-Arenesulfonylpyrroles were obtained in good yields from the reaction of pyrrolylpotassium with arenesulfonyl chlorides.

The reaction of pyrrolylpotassium with arenesulfenyl chlorides gave a mixture of 1-arenesulfenylpyrrole, 2-arenesulfenylpyrrole, and aryl disulfide.

Oxidation of the 1-arenesulfenylpyrroles yielded the expected 1-arenesulfonylpyrroles.

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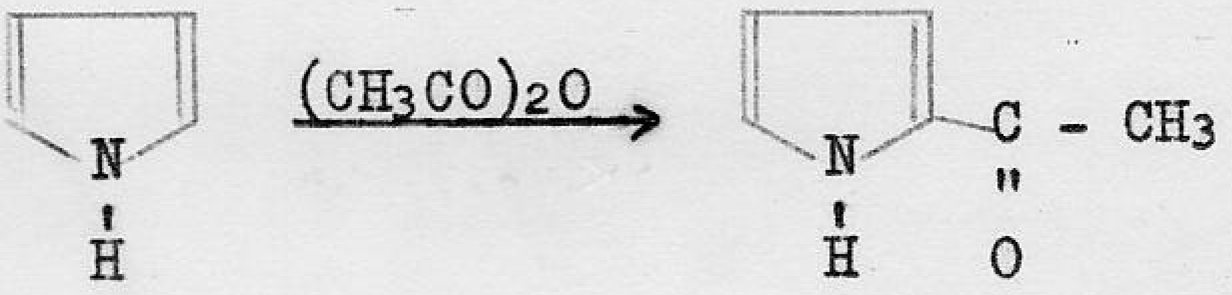
# INTRODUCTION

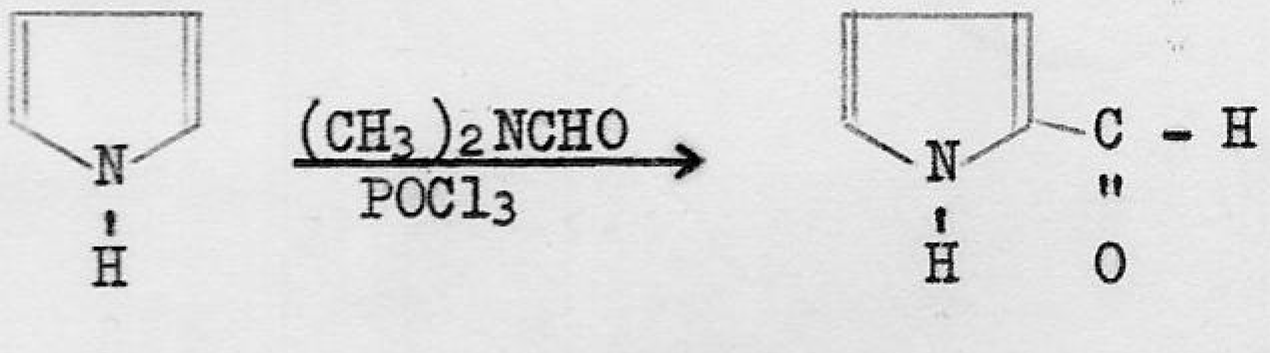
## 1. Pyrrole

As a heterocyclic analogue of cyclopentadiene, pyrrole possesses a sextet of $\pi$ electrons and, according to Hückel's rule, is aromatic. In fact, its most characteristic reactions are electrophilic substitution reactions in which the 2-position is predominantly involved.

In Friedel-Crafts reactions, 2-substituted derivatives are easily obtained and 2-acetylpyrrole is formed by heating pyrrole with acetic anhydride in the absence of a catalyst.[1]

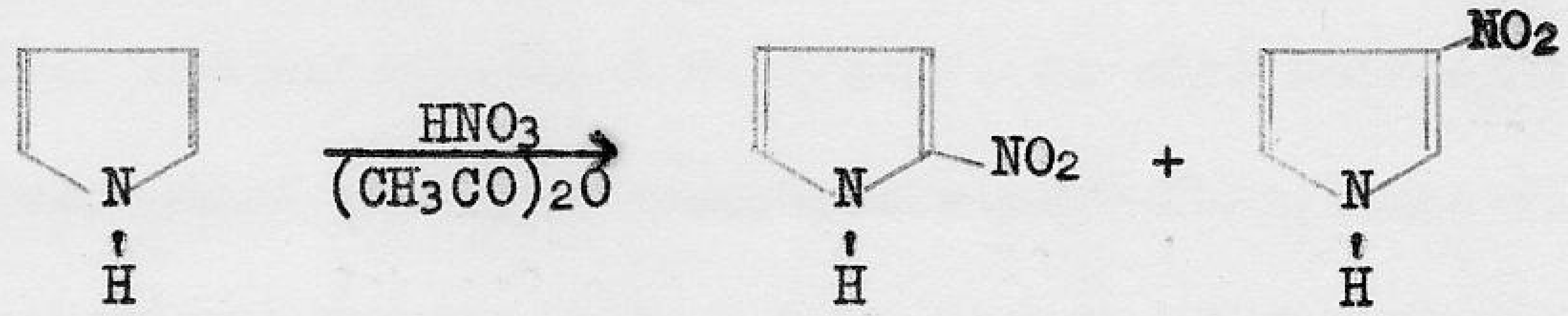


Pyrrole undergoes the Reimer-Tiemann reaction rather easily and yields the 2-formyl derivative. This latter compound is more conveniently prepared by the reaction of pyrrole with dimethylformamide in the presence of phosphorus oxychloride.[1]

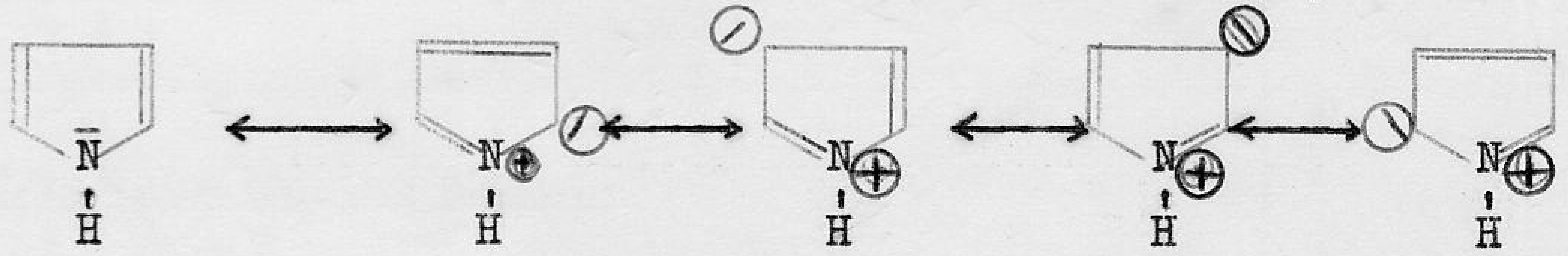


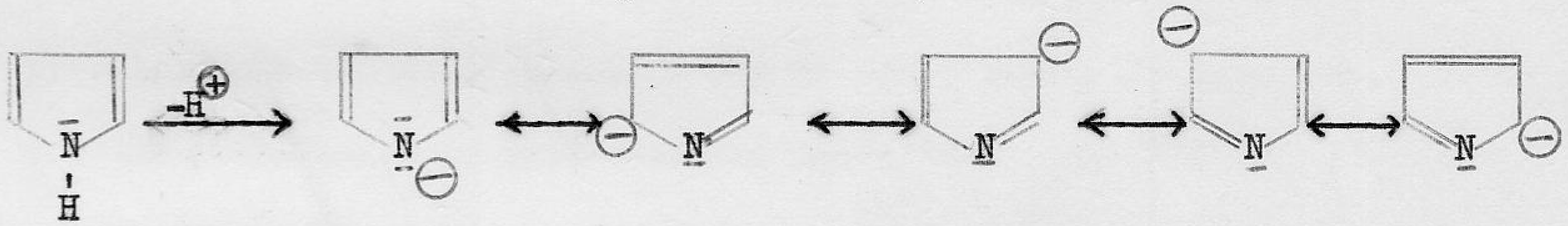
The nitration of pyrrole with fuming nitric acid and acetic anhydride yields mainly 2-nitropyrrole, but a small amount of the

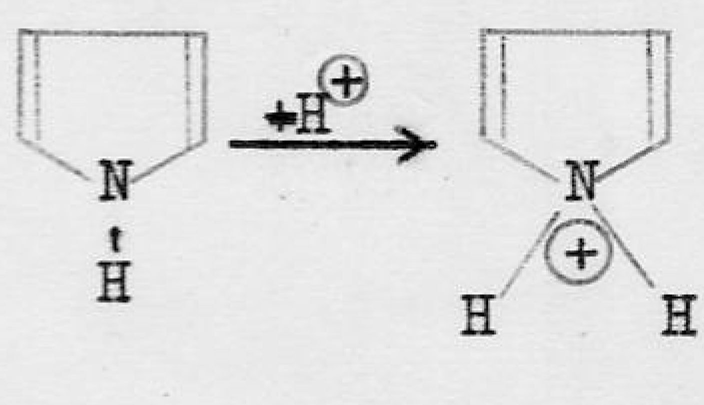
3-isomer is also formed.[2]



The reactions and properties of pyrrole are largely affected by its dual basic and acidic character due to the imino group. The acidic properties, however, are much more pronounced and this is to be expected on the basis of resonance considerations. The conjugate base of pyrrole is more resonance stabilized than pyrrole itself, whereas all resonance stabilization is lost in its conjugate acid.



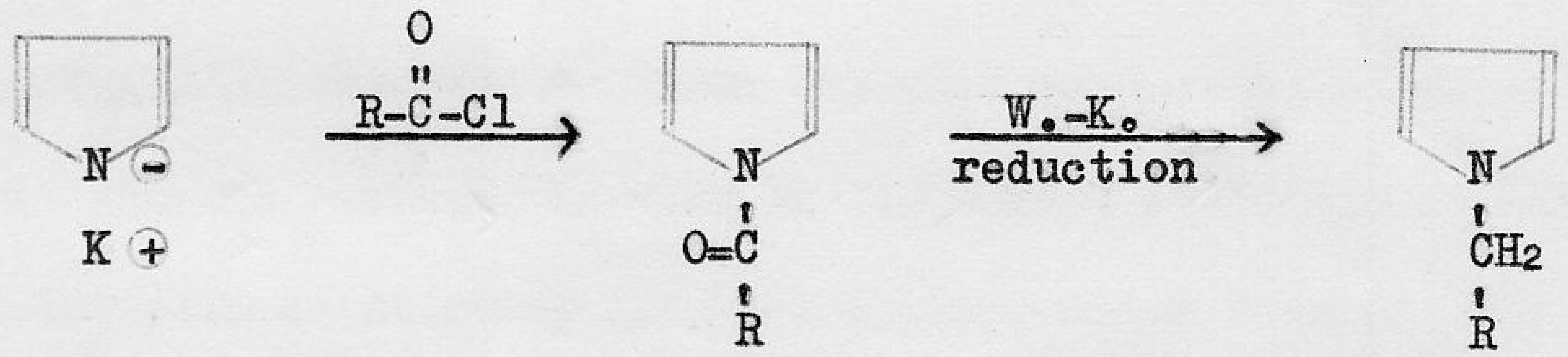




2. Pyrrolylpotassium

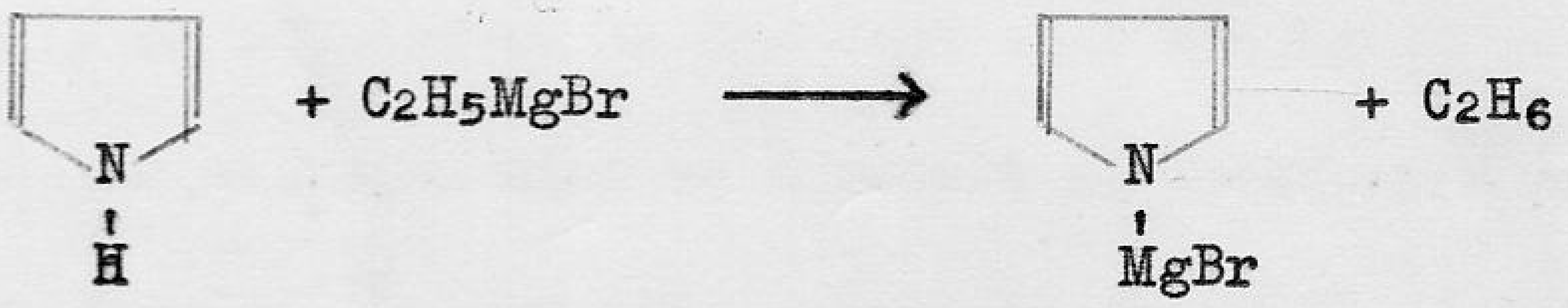
Pyrrole reacts readily with potassium to form pyrrolylpotassium with evolution of hydrogen:

This salt is the source of a large number of N-pyrrolyl derivatives and on treatment with alkyl or acyl halides it yields the corresponding N-alkyl or acylpyrroles. Thus, 1-acetylpyrrole and 1-benzoylpyrrole are prepared by the reaction of pyrrolylpotassium with the corresponding acyl halides.[3] Reduction of the 1-pyrrolylketones, usually by the Wolff-Kishner method, affords the corresponding 1-alkylpyrroles.

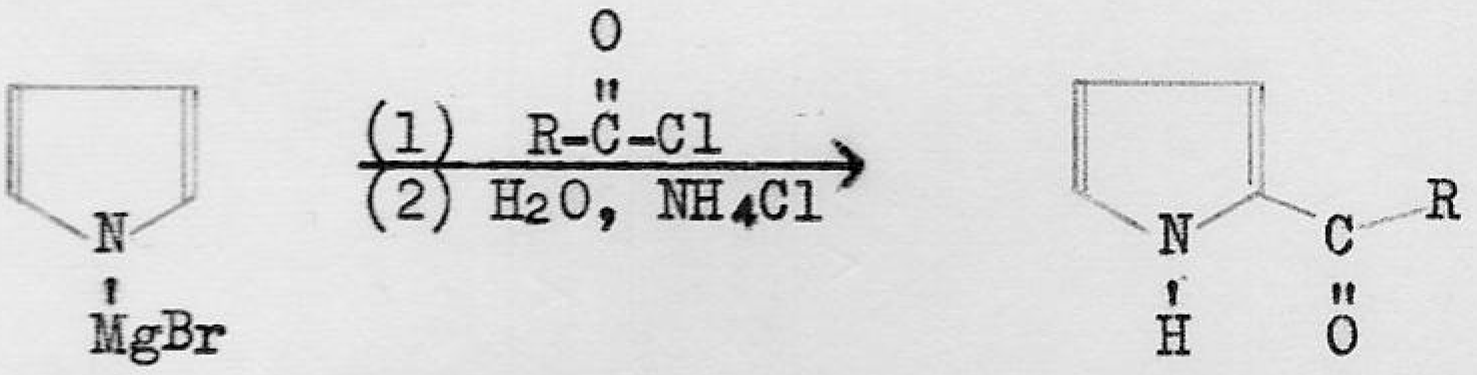


3. Pyrrolylmagnesium bromide

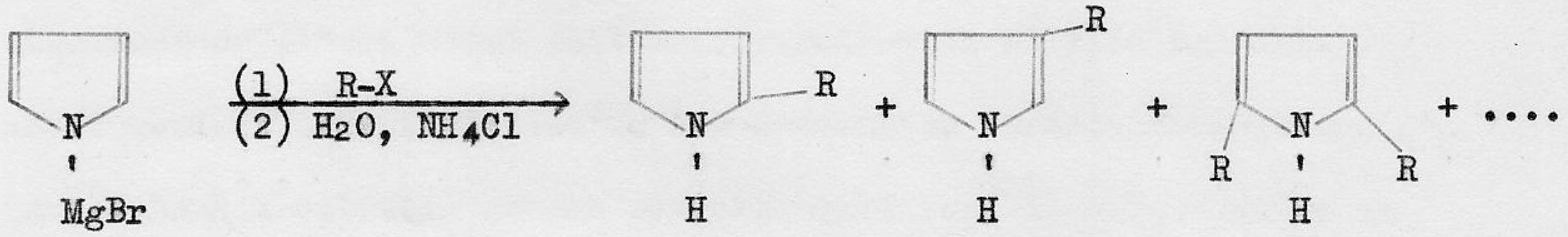
Pyrrole reacts readily with organomagnesium halides, and the pyrrolylmagnesium halides formed are valuable synthetic reagents for the preparation of C-substituted pyrroles.



More particularly, pyrrolylmagnesium halides react, in relatively clean reactions, with acyl halides to give 2-acylpyrroles thus supplying a good method for the synthesis of 2-pyrrolylketones.



The action of alkyl halides on pyrrolylmagnesium halides is more complicated, however; and although the major component of the product is the 2-alkylpyrrole, there are also smaller amounts of the 3-isomer and dialkylpyrroles.[4,5]

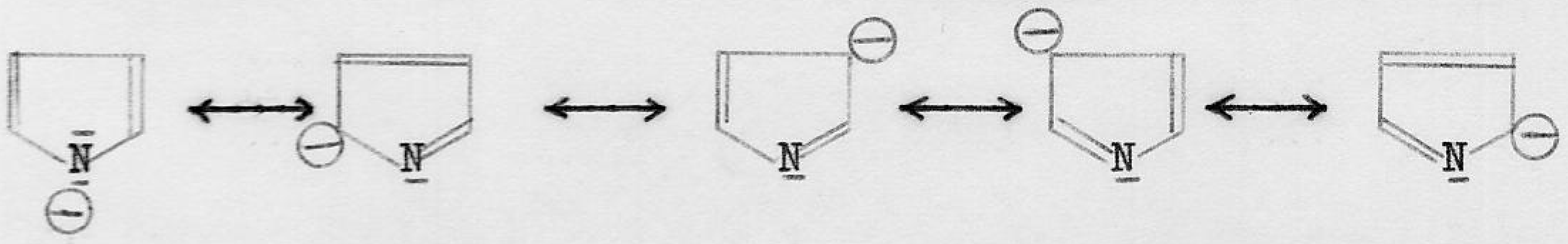


The controversy[4,6,7] about the position of the magnesyl group on the pyrrole nucleus, in view of the almost exclusive formation of C-derivatives starting from pyrrolylmagnesium bromide, was resolved recently when infrared spectra and nuclear magnetic resonance studies proved that pyrrolylmagnesium bromide consists of an -NMgBr or ionic species both in ether and tetrahydrofuran.[8,9]

The preference for substitution on carbon atoms should probably be attributed to the fact that the $\overset{+}{MgBr}$ group effectively blocks the nitrogen atom as a result of incomplete dissociation of the salt caused by the low dielectric constant of ether.[5]

## 4. The Pyrrolyl ambident anion

As expected from its resonance structures, the pyrrolyl anion



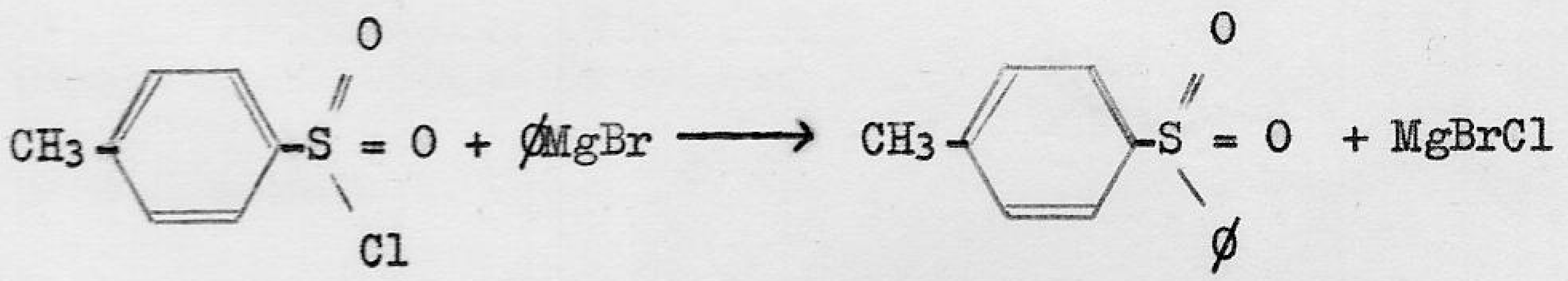
is an ambident anion which can undergo covalent bond formation at any of the five positions in the ring.

The factors that affect the position of substitution of ambident ions are many and their effect is complicated and difficult to interpret.

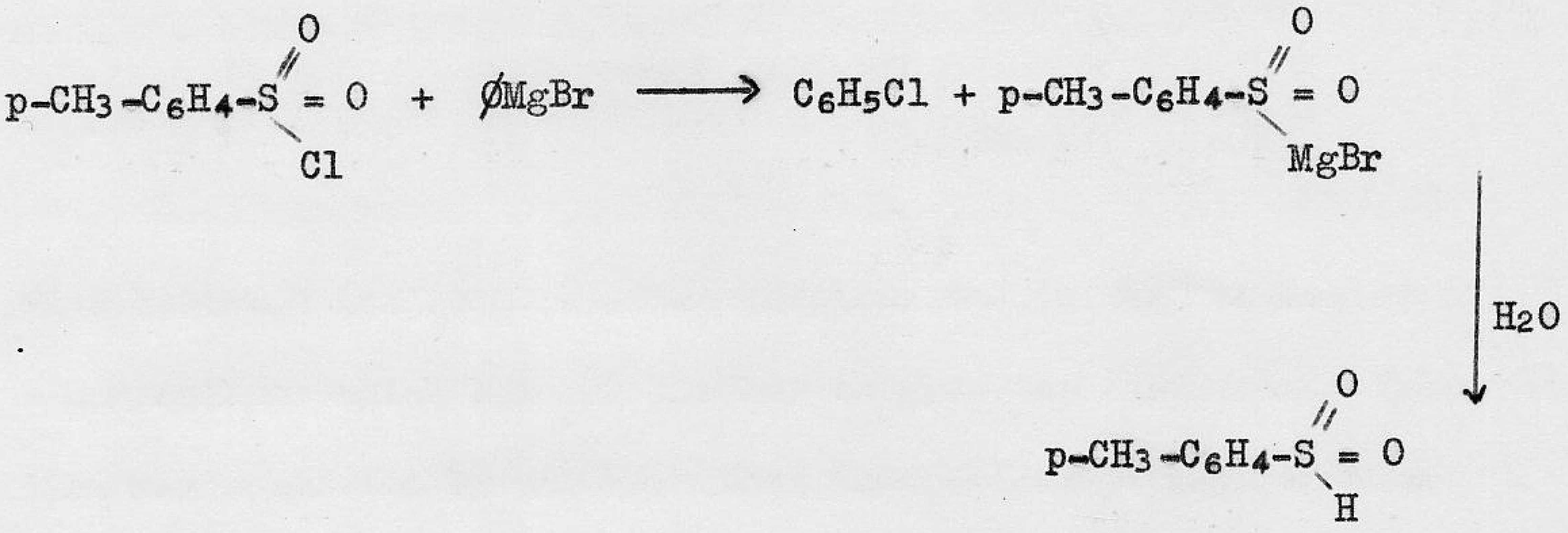
In the case of the pyrrolyl anion, a study of the alkylation reactions of alkali metal salts of pyrrole with allylic halides under various conditions led to the conclusion that factors which favor the dissociation of the pyrrolyl salt lead to substitution at the nitrogen atom. On the other hand, factors which favor the association of the pyrrolyl salt lead to carbon substitution.[10] The same conclusion was arrived at by a study of the alkylation of pyrrolyl salts with alkyl sulfonates.[11]

## 5. Reactions of carbanions with sulfonyl halides

In a systematic study of the reactions of various sulfonyl chlorides with organomagnesium halides, Gilman and Fothergill[12] showed that the chief products of these reactions are sulfones, sulfinic acids and alkyl chlorides where the alkyl group is that of the Grignard reagent. They attributed the formation of the sulfone to a direct substitution:



They further postulated that the sulfinic acid and the alkyl chloride are formed by another direct substitution as a result of which the chlorine atom of the sulfonyl chloride is replaced by the - MgX group.



$$p\text{-}CH_3\text{-}C_6H_4\text{-}\overset{\overset{O}{\|}}{\underset{Cl}{S}}=O + \phi MgBr \longrightarrow C_6H_5Cl + p\text{-}CH_3\text{-}C_6H_4\text{-}\overset{\overset{O}{\|}}{\underset{MgBr}{S}}=O \xrightarrow{H_2O} p\text{-}CH_3\text{-}C_6H_4\text{-}\overset{\overset{O}{\|}}{\underset{H}{S}}=O$$

In a similar study of the reactions of sulfonyl halides with Grignard reagents, Burton and Davy obtained sulfones at low temperatures, and sulfoxides at higher temperatures.[13]

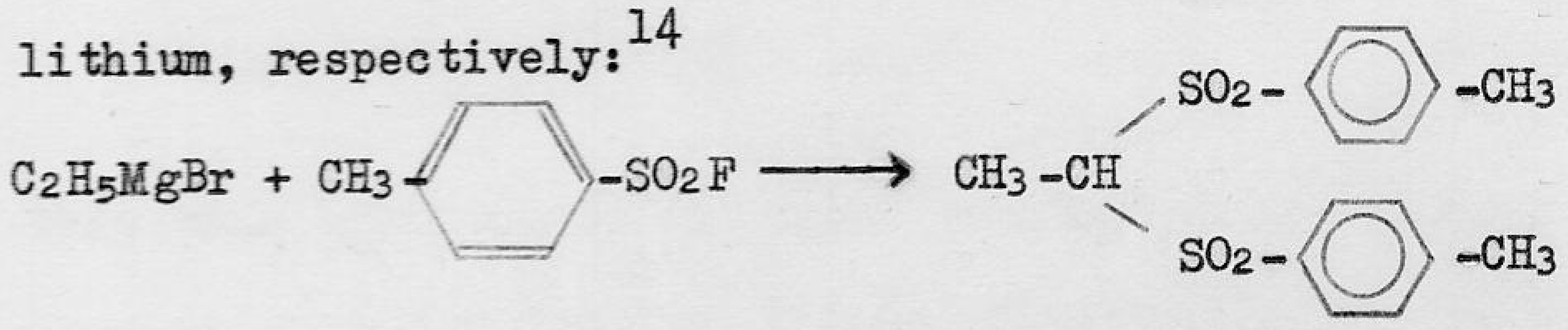
$$p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2Cl + \phi MgBr \xrightarrow{-10^\circ \text{ to } -5^\circ C} \phi Cl + \phi\text{-}\phi + p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2\phi$$

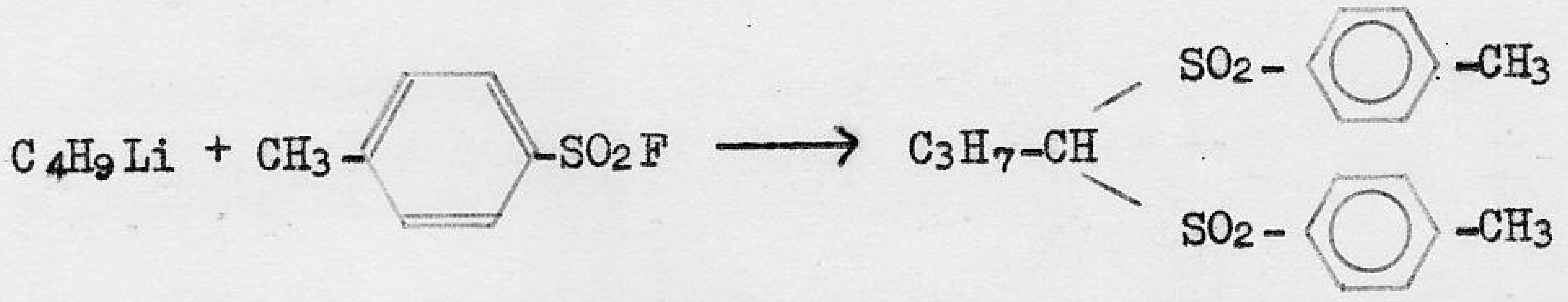
$$p\text{-}CH_3\text{-}C_6H_4\text{-}SO_2Cl + \phi MgBr \xrightarrow[\text{benzene}]{\text{reflux}} \phi OH + \phi Cl + \phi\text{-}\phi + CH_3\text{-}C_6H_4\text{-}SO\phi$$

They explained the formation of the sulfoxides as follows:

$$ArSO_2MgBr \xrightarrow{\phi MgBr} ArS\phi(OMgBr)_2 \longrightarrow ArS\phi(OH)_2 \longrightarrow ArSO\phi + H_2O$$

Fukuda and coworkers obtained 1,1-bis-(p-toluenesulfonyl) ethane and 1,1-bis-(p-toluenesulfonyl) butane when they treated p-toluenesulfonyl fluoride with ethylmagnesium bromide and n-butyl lithium, respectively:[14]





They believed that the reaction involved the initial formation of a monosulfone which reacted further to give the disulfone. This view was supported by the fact that independently prepared monosulfone reacted with the organometallic compound and p-toluenesulfonyl fluoride to form the disulfone.

Very recently, Shirota and coworkers treated benzylsulfonyl chloride with phenyl lithium and obtained a product containing eight compounds among which $\phi CH_2SO_2\phi$ was in only 0.4% yield.[15]

6. Substitution reactions of sulfenyl halides

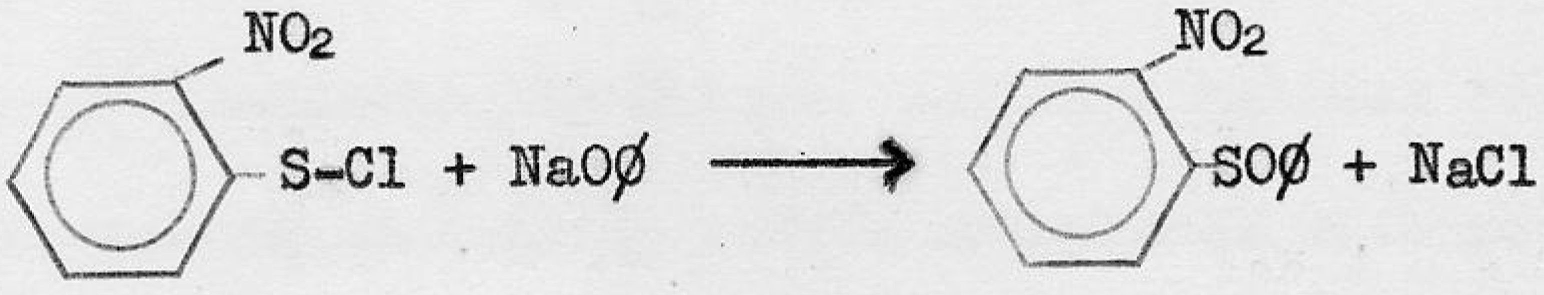
Aryl sulfenyl chlorides undergo substitution reactions with a large variety of nucleophilic reagents. Thus with silver salts of sulfinic acids, they give disulfoxides in almost quantitative yields.[16]

$$\phi SO_2Ag + \phi SCl \longrightarrow \phi S_2O_2\phi + AgCl$$

With silver nitrate, sulfenyl nitrates are formed.[17]

$$ArSCl + AgNO_3 \xrightarrow{CH_3CN} ArSONO_2 + AgCl$$

They react with sodium alkoxides and phenoxides to form the corresponding alkyl and aryl sulfenates.[16]



Quite recently, Moore and O'Connor treated methylsulfenyl chloride with lithium alkoxides and obtained the methyl sulfenates.[18]

$$\text{CH}_3\text{SCl} + \text{LiOR} \xrightarrow[-20^\circ \text{ to } -60^\circ\text{C}]{\text{D. M. E.}} \text{CH}_3\text{SOR} + \text{LiCl}$$

They observed, however, that with excess methylsulfenyl chloride the sulfinate esters, $\text{CH}_3\text{SO}_2\text{R}$, are formed.

Sulfenyl halides also react readily with potassium cyanide to give thiocyanates and with mercaptides to form disulfides.[16]

As early as 1925 Lecher and coworkers found that treatment of benzenesulfenyl chloride or p-toluenesulfenyl chloride with phenylmagnesium bromide gives the corresponding sulfide.[16]

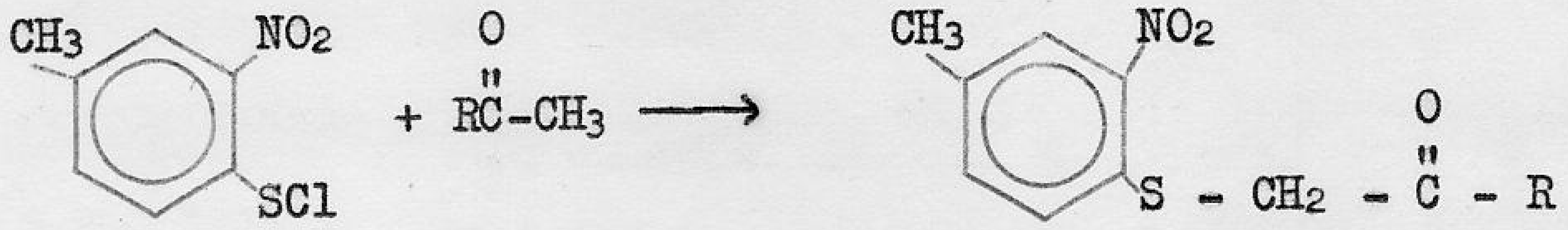
$$\phi\text{MgBr} + \text{ArSCl} \longrightarrow \phi\text{SAr} + \text{MgBrCl}$$

Similarly, in 1964, Sheppard obtained good yields of aryl trifluoromethyl sulfides by the reaction of aryl Grignard reagents with trifluoromethanesulfenyl chloride.

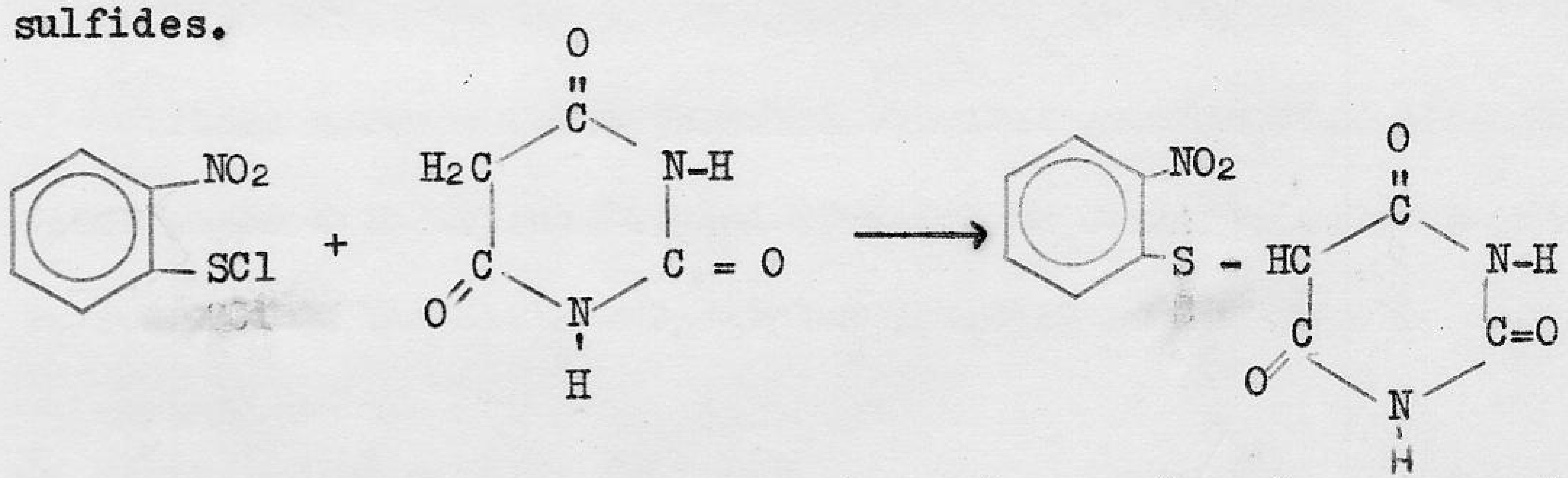
$$\text{ArMgX} + \text{CF}_3\text{SCl} \longrightarrow \text{ArSCF}_3 + \text{ArCl} + \text{ArX}$$

On the other hand, the reaction of trifluoromethanesulfenyl chloride with phenyl lithium gave a low yield and much tar.[19] No definite products were isolated from the similar reaction of phenylmagnesium bromide with trichloromethanesulfenyl chloride which was reported to be highly exothermic.[20]

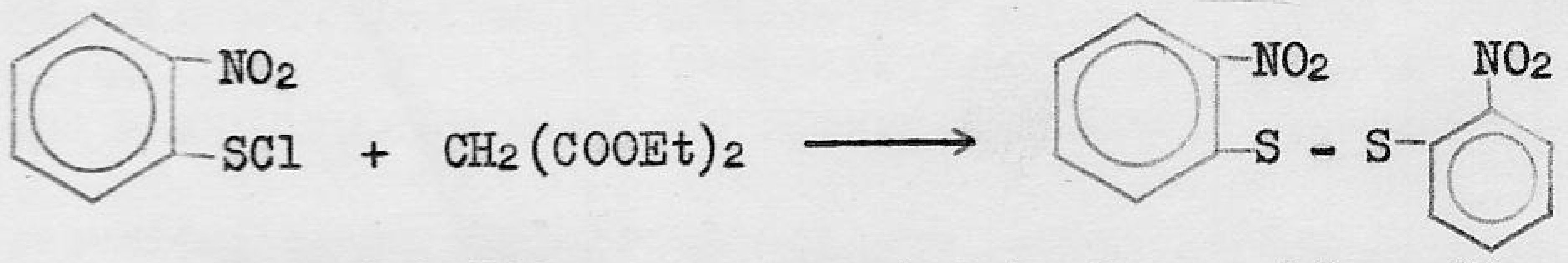
According to Zincke, sulfenyl halides react with ketones and compounds containing active methylenes with replacement of the hydrogen of the active methylene by an - ArS group.[16]



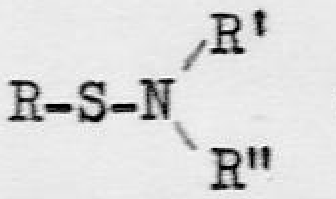
In 1966, Coutts and coworkers treated active methylene compounds with o-nitrobenzenesulfenyl chloride and obtained the corresponding sulfides.



Similar treatment, however, of $CH_2(COOEt)_2$, $CH_2(COOH)_2$ and $EtCH(COOH)_2$ with o-nitrobenzenesulfenyl chloride yielded o-nitrophenyldisulfide.[21]



Sulfenyl halides are reported to form sulfenamides by the reaction with ammonia, primary, and secondary amines. In this way, Zincke and coworkers prepared sulfenamides of the general structure

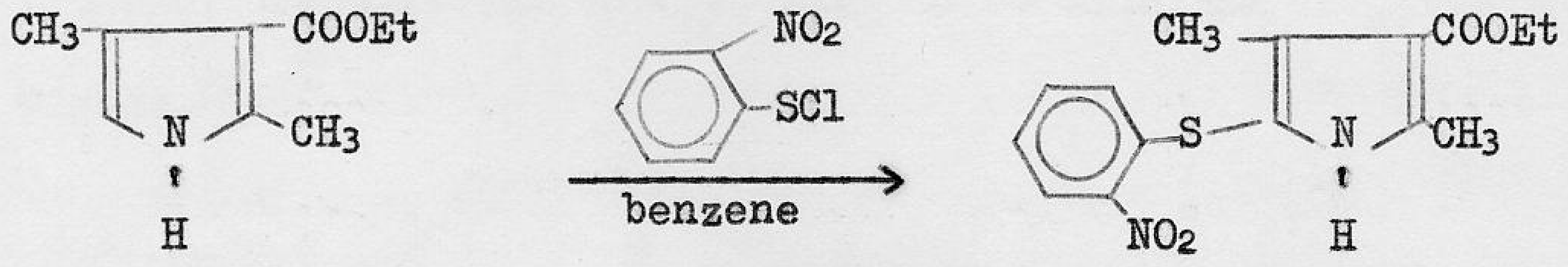


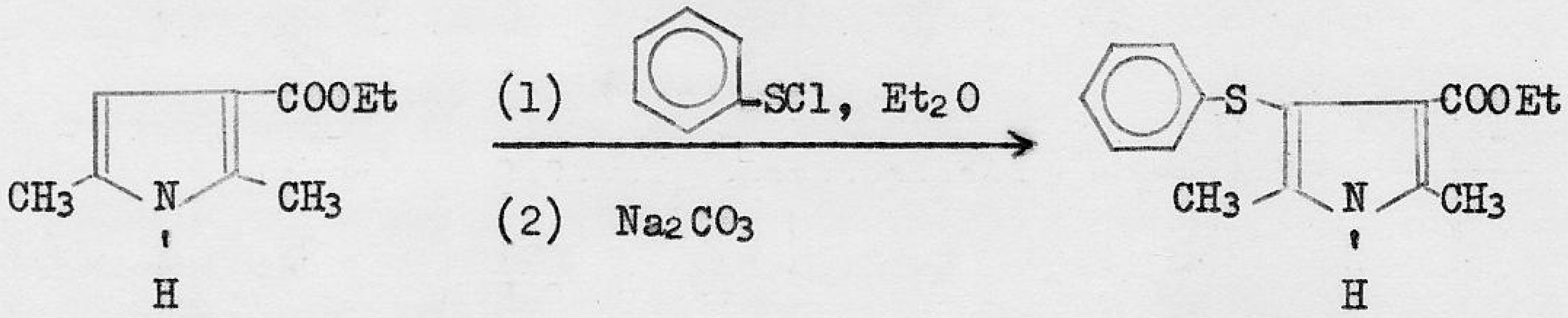
$R\text{-}S\text{-}N\begin{smallmatrix}R'\\R''\end{smallmatrix}$

where R, R', R" are aliphatic, alicyclic, or heterocyclic.[16,22]

$$RSX + 2HNR_2 \longrightarrow RSNR_2 + R_2\overset{+}{N}H_2\overset{-}{X}$$

The reaction of sulfenyl chlorides with substituted pyrroles was studied by Fischer and coworkers.[23,24]





These workers found that the expected substitution reaction takes place with trisubstituted pyrroles to form the corresponding sulfides, but that tetrasubstituted pyrroles do not react.

## 7. Oxidation of organic sulfides

Various oxidizing agents have been used for the oxidation of organic sulfides to sulfoxides and sulfones. The most efficient and most commonly used are peroxy compounds such as hydrogen peroxide, alkyl hydroperoxides and peroxy acids.

Oxidations of sulfides to sulfoxides with $H_2O_2$ are very common in the literature and the yields are usually satisfactory.[25,26,27,28]

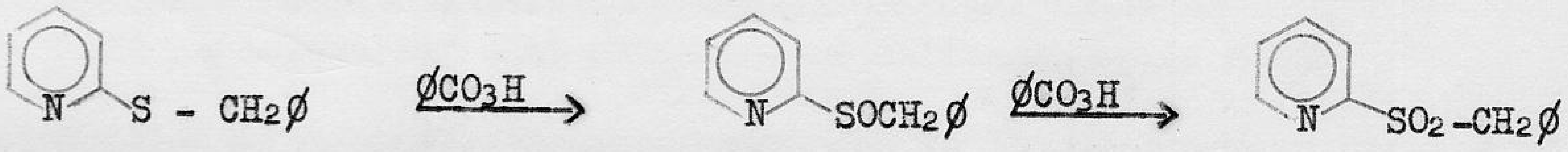
$$CH_2{=}CH{-}CH_2{-}S{-}C_6H_5 \xrightarrow{H_2O_2} CH_2{=}CH{-}CH_2{-}SO{-}C_6H_5$$

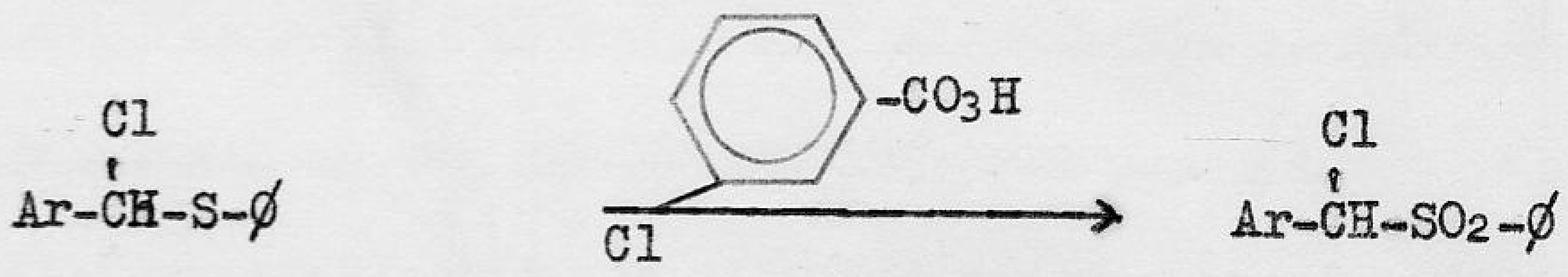
With a larger amount of peroxide and occasionally higher temperature, the sulfones are reported to be obtained in satisfactory yields.[29,30]

$$\phi CH_2\text{-}S\text{-}CH_2\phi \xrightarrow[10^{\circ}C]{30\%\ H_2O_2} \phi CH_2SOCH_2\phi$$

$$\phi CH_2\text{-}S\text{-}CH_2\phi \xrightarrow[95^{\circ}C]{30\%\ H_2O_2} \phi CH_2SO_2CH_2\phi$$

Peroxy acids, and particularly perbenzoic acid and its deactivated ring derivatives, have also been widely used for the oxidation of organic sulfides.[31,32]





Organic hydroperoxides usually oxidize organic sulfides to the sulfoxide stage only. Recently, however, Kuhnen obtained high yields of sulfones by the use of metal oxides as catalysts.[33]

$$\phi\text{-}S\text{-}CH_3 \xrightarrow[\text{molybdenyl acetylacetonate}]{\text{t-BuOOH}} \phi\text{-}SO_2\text{-}CH_3 \qquad 98\%$$

$$CH_3SOCH_3 \xrightarrow[V_2O_5]{\text{cumyl hydroperoxide}} CH_3SO_2CH_3 \qquad 91\%$$

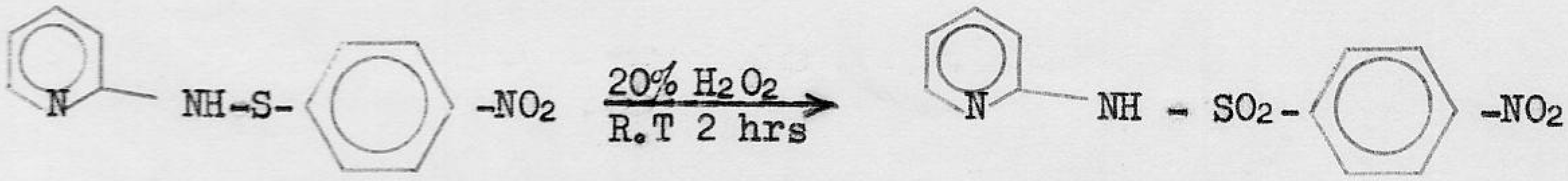
Other oxidizing agents that have occasionally been used with good results include chromic anhydride, potassium permanganate, and nitric acid.[25]

$$\text{Dibenzyl sulfide} \xrightarrow{CrO_3} \text{dibenzyl sulfone}$$

$$\text{Bis-n-butyl sulfide} \xrightarrow[\text{ACOH, 2N } H_2SO_4]{KMnO_4} \text{Bis-n-butyl sulfone}$$

$$\text{Bis-n-butyl sulfide} \xrightarrow[0^\circ C]{HNO_3} \text{Bis-n-butyl sulfoxide}$$

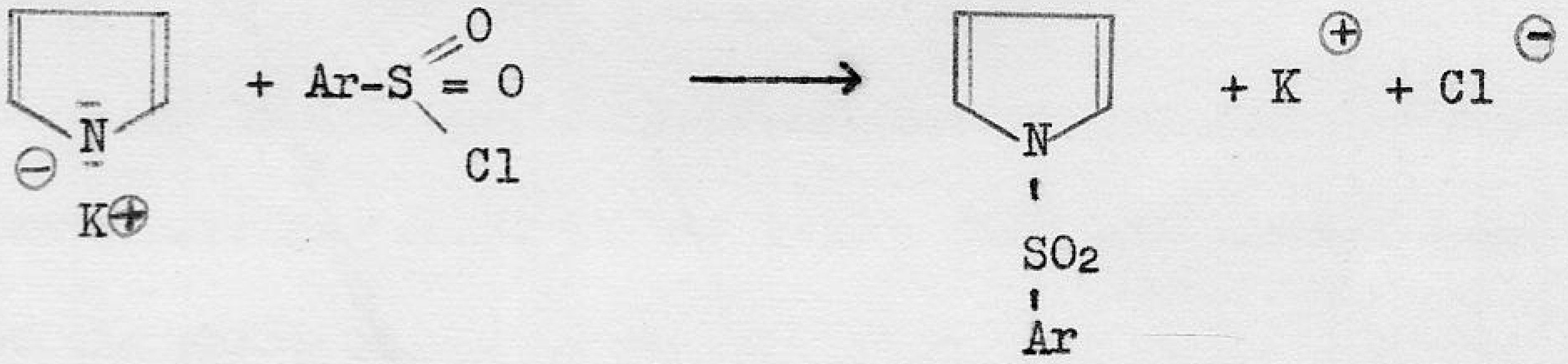
It is noteworthy that oxidation of sulfenamides is often accompanied by molecular rearrangement due to the cleavage of the -S-N- bond during the oxidation process. Lorenz and coworkers, however, were able to transform sulfenamides to the corresponding sulfonamides by the use of 20% hydrogen peroxide at room temperature, potassium permanganate in alkaline medium, or sodium dichromate in acetic acid at room temperature.[22]



## DISCUSSION

The purpose of this work was the synthesis of a series of 1-, and 2- arenesulfonylpyrroles and 1-, and 2-arenesulfenylpyrroles, followed by the oxidation of the sulfenyl to the sulfonyl derivatives for structural correlation.

The first part of the project was carried out successfully by the reaction of pyrrolylpotassium with arenesulfonyl chlorides in tetrahydrofuran, a nucleophilic substitution reaction in which the pyrrolyl anion displaces the weaker base, chloride ion, to form the arenesulfonylpyrrole.



The following arenesulfonylpyrroles were prepared in good yields by this method:

1-benzenesulfonylpyrrole

1-(p-toluenesulfonyl) pyrrole

1-(p-bromobenzenesulfonyl) pyrrole

1-(p-acetaminobenzenesulfonyl) pyrrole

1-(p-aminobenzenesulfonyl) pyrrole

1-(α-naphthalenesulfonyl) pyrrole

1-($\beta$-naphthalenesulfonyl) pyrrole

The assignment of the structure of 1-arenesulfonylpyrrole to the above compounds is supported by the following facts:

a) In each case, the elemental analysis agreed with the calculated composition.

b) Except in the cases of 1-(p-acetaminobenzenesulfonyl) pyrrole and 1-(p-aminobenzenesulfonyl) pyrrole, the infrared spectra showed complete absence of absorption in the 3400 - 3500 $cm^{-1}$ region (pyrrole N-H stretching)[34] thus excluding the possibility of the presence of 2- or 3-substituted pyrrole derivatives.

c) In all cases, the infrared spectrum had a strong band in the range 1130 - 1170 $cm^{-1}$ ($-SO_2-$ group)[35] and a very strong band in the range 1350 - 1380 $cm^{-1}$ ($-SO_2-N\langle$ group).[35]

d) In the case of 1-(p-aminobenzenesulfonyl) pyrrole there were two absorption bands in the 3350 - 3450 $cm^{-1}$ region ($-NH_2$ stretching)[36] of the spectrum.

Further evidence for the structure of 1-(p-aminobenzenesulfonyl) pyrrole was provided through its conversion by acetylation to 1-(p-acetaminobenzenesulfonyl) pyrrole in high yield.

In contrast to the 1-derivatives, 2-arenesulfonylpyrroles proved unexpectedly difficult to obtain, and all attempts at their preparation were unsuccessful. There are examples in the literature of preparation of sulfones in low to moderate yields by the reaction of Grignard reagents with arenesulfonyl halides.[12,13,14] In this work, however, pyrrolylmagnesium bromide yielded only tars when treated with sulfonyl chlorides. It was hoped that a Friedel-Crafts type sulfonylation might give acceptable results, but polymerization of pyrrole could not be prevented, even when $ZnCl_2$ was used as a catalyst. When Friedel-Crafts type reactions were carried out on 1-pyrrolecarboxanilide, the pyrrole ring of which would be expected to be less sensitive to acids, the reaction either did not take place at all, or led to polymerization. Pyrrole has been observed to be easily carbon alkylated by treatment with reactive alkyl halides, if polymerization is prevented by the presence of a base.[37] Analogous reactions failed in the present case. Finally, attempts to utilize the known reactivity of N-amides and N-esters of imidazole in nucleophilic substitutions[38] were also fruitless as reactions between 1-(p-toluenesulfonyl) imidazole and pyrrole failed.

The preparation of arenesulfenylpyrroles also proved more difficult than had been anticipated. Only two such compounds were obtained in acceptable yields and were characterized satisfactorily. 1-benzenesulfenylpyrrole and 1(p-toluenesulfenyl) pyrrole were prepared by the reaction of pyrrolylpotassium with the corresponding sulfenyl halides in tetrahydrofuran and the structures were assigned to them on the basis of the following evidence:

a) The elemental analyses agreed with the calculated compositions.

b) There was no NH stretching absorption peak in their infrared spectra.

c) Oxidation led to the expected 1-benzenesulfonylpyrrole and

1-(p-toluenesulfonyl) pyrrole, respectively.

From the product of the reaction of pyrrolylpotassium with benzenesulfenyl chloride a compound was isolated, with a b.p. higher than that of 1-benzenesulfenylpyrrole, which analyzed correctly for a benzenesulfenylpyrrole. Since it shows a sharp absorption band at 3320 $cm^{-1}$, this is very likely 2-benzenesulfenylpyrrole, but the presence, in it, of the 3-isomer cannot be entirely excluded. It is known that treatment of pyrrolylpotassium with reactive alkyl (e.g. allylic) halides yields, in addition to 1- and 2-alkylpyrroles, smaller amounts of the 3-isomer.[37] However, the fact that thin layer chromatography of the above compound on silica gel with benzene, a 50:50 benzene-chloroform mixture, or chloroform as the eluants, showed only one spot suggests that, if any, the proportion of 3-benzenesulfenylpyrrole must be very small.

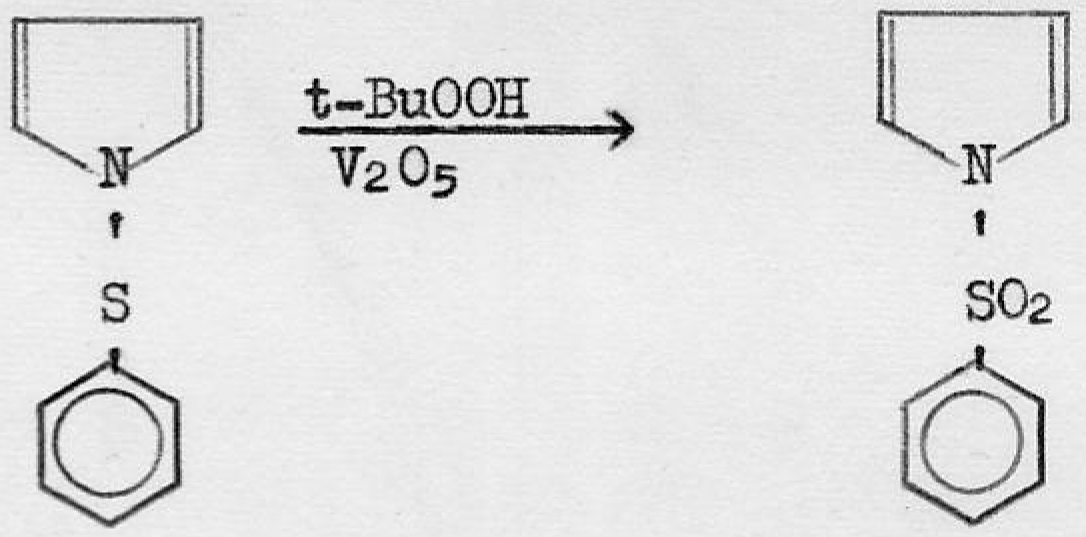
A higher boiling fraction was also isolated from the product of the reaction with p-toluenesulfenyl chloride, but this was a mixture as shown by its wide boiling point range. The infrared spectrum of the originally collected fraction, a low melting solid, contained a strong pyrrole N-H absorption peak, but on successive recrystallizations this peak disappeared, and p-tolyl disulfide was isolated. Because of the considerable polymerization which accompanied the distillation, the amounts of distillate collected were quite small, and it was not considered practical to use chromatography to separate the components of this mixture.

The formation of the disulfide as a by-product was observed in the reaction of pyrrolylpotassium with benzenesulfenyl chloride, too.

There are several examples in the literature of the formation of disulfides as by-products of reactions of sulfenyl chlorides.[16,21]

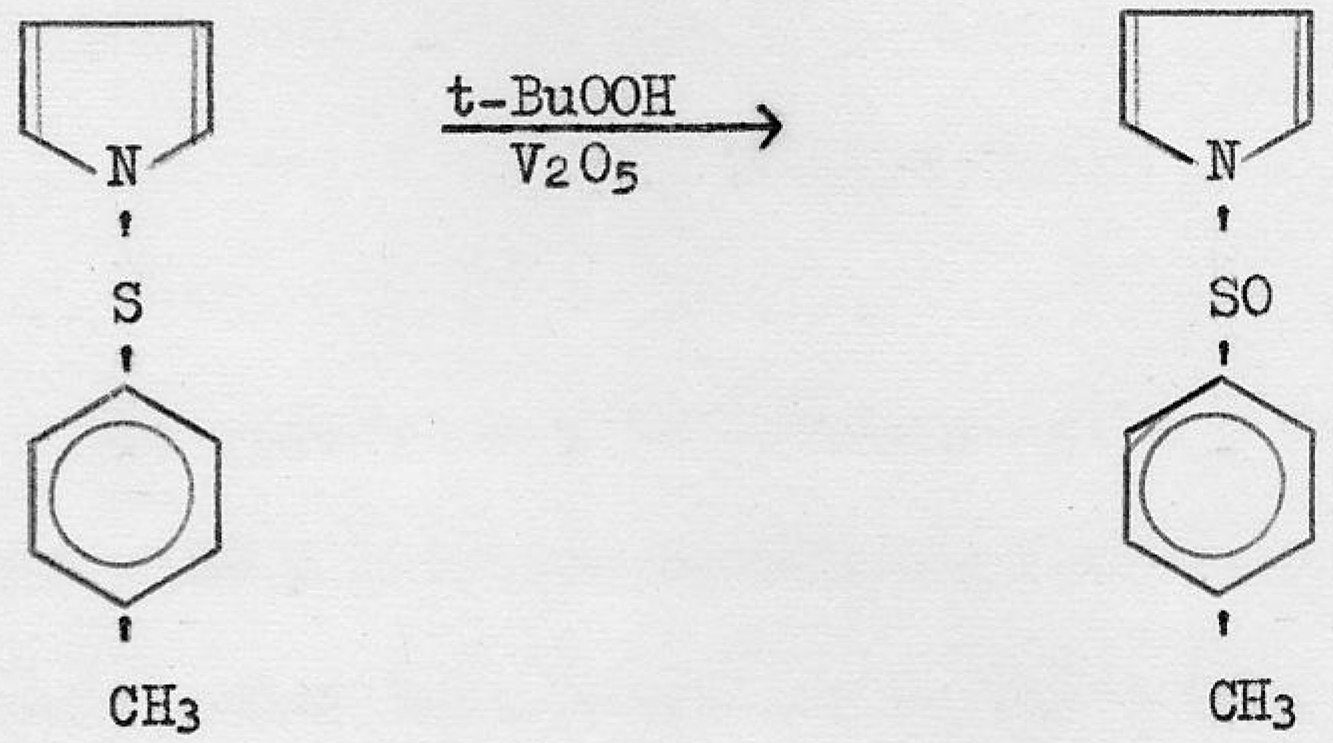
When pyrrolylmagnesium bromide was made to react with benzene- or p-toluenesulfenyl chloride, the product was a rather complex mixture the components of which could not be separated by fractional distillation. No information about the composition of these mixtures could be obtained by vapor-phase chromatography, because the compounds contained in them decomposed inside the columns used. Thin layer chromatography showed the presence of at least three compounds in each mixture.

Oxidation of 1-benzenesulfenylpyrrole with tert-butyl hydroperoxide, in the presence of vanadium pentoxide, yielded 1-benzenesulfonylpyrrole in low yield.

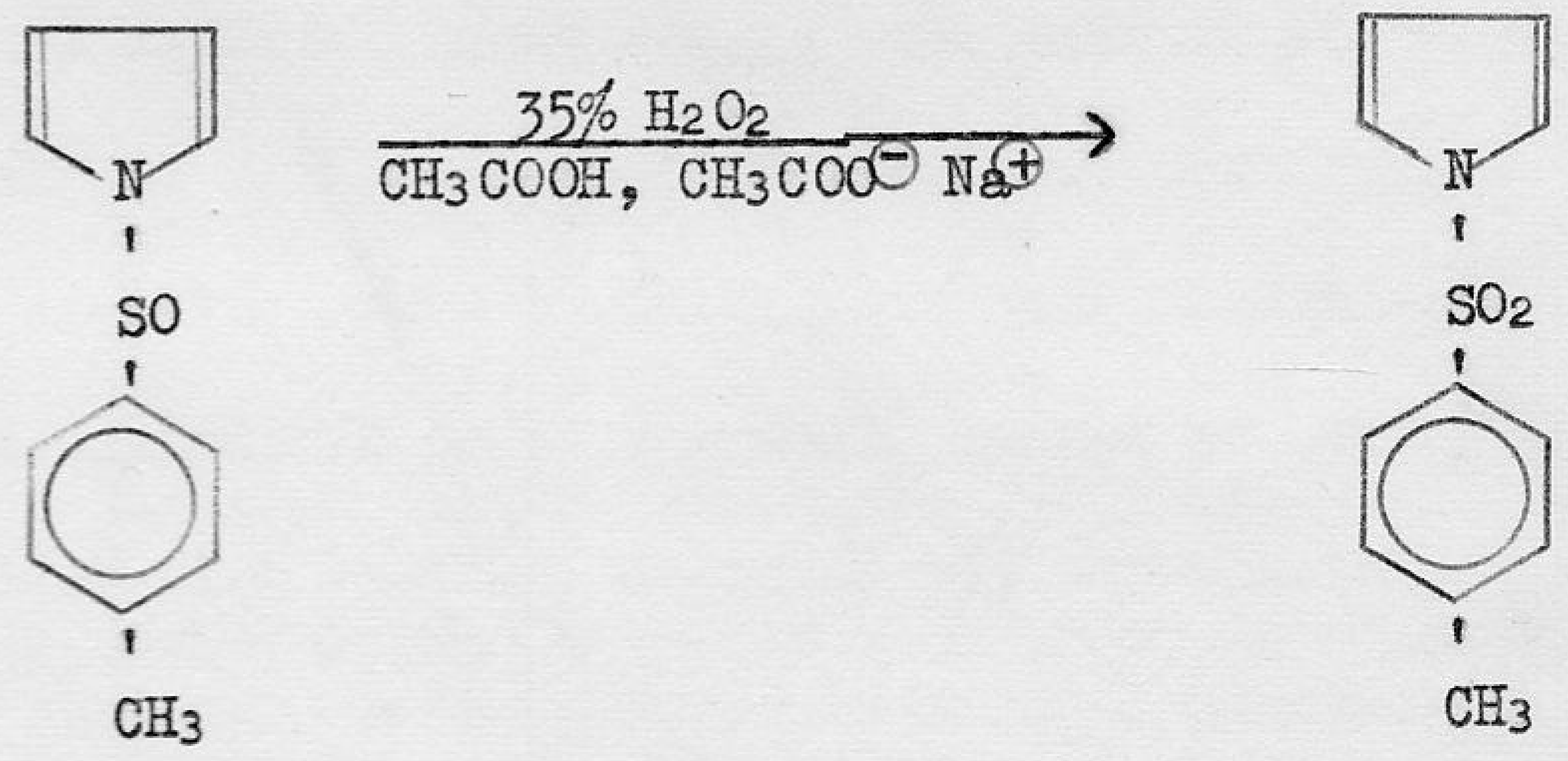


No product could be isolated when hydrogen peroxide was used as the oxidant.

In the case of 1-(p-toluenesulfenyl) pyrrole, oxidation with tert-butyl hydroperoxide and vanadium pentoxide stopped at the 1-(p-toluenesulfinyl) pyrrole stage, contrary to the behavior of other sulfides which have been observed to yield the sulfones under the same conditions.[33]



The structure assigned to the product of this reaction is supported by its elemental analysis, its infrared spectrum which contains an absorption band at 1040 cm$^{-1}$ (-$\overset{O}{\overset{\|}{\text{S}}}$- group)[35], and its further oxidation to 1-(p-toluenesulfonylpyrrole) with hydrogen peroxide in the presence of acetic acid and sodium acetate.



# EXPERIMENTAL

The apparatus used consisted of a 500 ml three necked flask fitted with a pressure equalizing funnel, a sleeve type stirrer, and a water cooled bulb condenser to the top of which was fitted a small calcium chloride tube.

## Preparation of 1-arenesulfonylpyrroles

### General Procedure

To a solution of a small excess of pyrrole in tetrahydrofuran[a] was added potassium, freshly cut into small pieces under kerosene and washed with tetrahydrofuran. The mixture was refluxed with stirring until all the potassium had reacted. Heating was then stopped and the reaction mixture was diluted with additional solvent[a]. A solution, in tetrahydrofuran[a], of a molar amount of sulfonyl chloride slightly smaller than that of potassium was subsequently introduced dropwise, and the mixture was stirred at room temperature for an average of 14 - 18 hours. Filtration of the product, followed by ether washing of the residue yielded a solution which was evaporated to dryness under reduced pressure.

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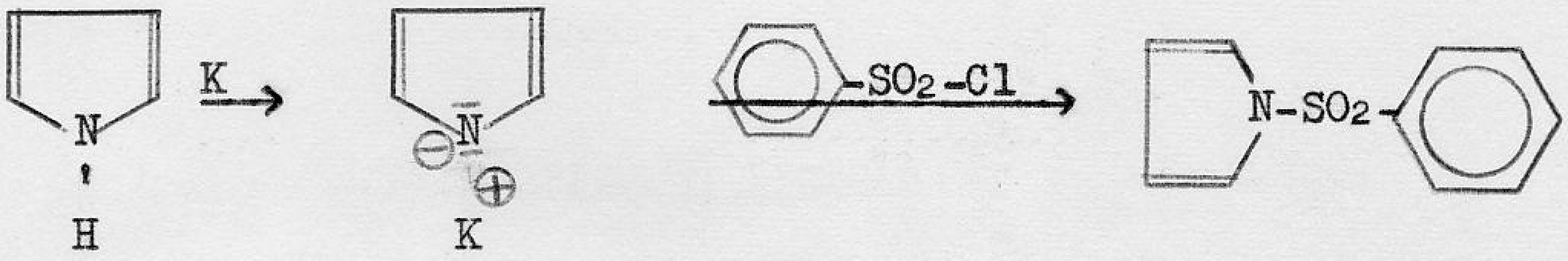
[a] The solvent, introduced in three equal parts as indicated above, totalled 300 ml in reactions involving 0.22 mole of the sulfonyl chloride, and 150 ml in reactions with 0.11 mole or 0.1 mole of the chloride.

### 1. 1-Benzenesulfonylpyrrole



From 18.76 g (0.28 mole) of pyrrole, 9.75 g (0.25 mole) of potassium, and 38.8 g (0.22 mole) of benzenesulfonyl chloride, 39.8 g (87.4%) of crude product, m.p. 82 - 84°, was obtained. One recrystallization from methyl alcohol yielded 34.2 g of white crystals melting at 84 - 85°.

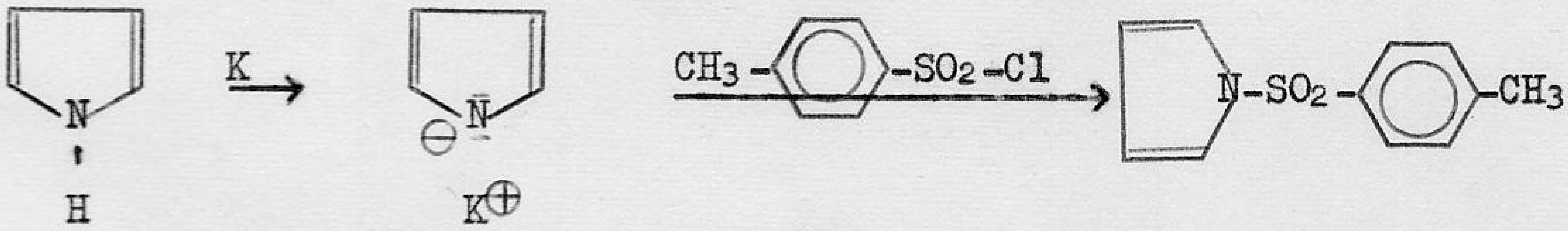
(M.p. of an analytical sample: 86°).

Anal. Calcd. for $C_{10}H_9NO_2S$: C, 57.97; H, 4.38, N, 6.76; S, 15.45.

Found: C, 58.10; H, 4.32; N, 6.87; S, 15.60.

IR Spectrum No. 1

### 2. 1-(p-Toluenesulfonyl) pyrrole



The same quantities as above were used. The yield in crude product, m.p. 98.5 - 99.5°, was 41.0 g (84.3%). One recrystallization from methyl alcohol gave 38.9 g of white crystals melting at 100.5 - 101.5°.

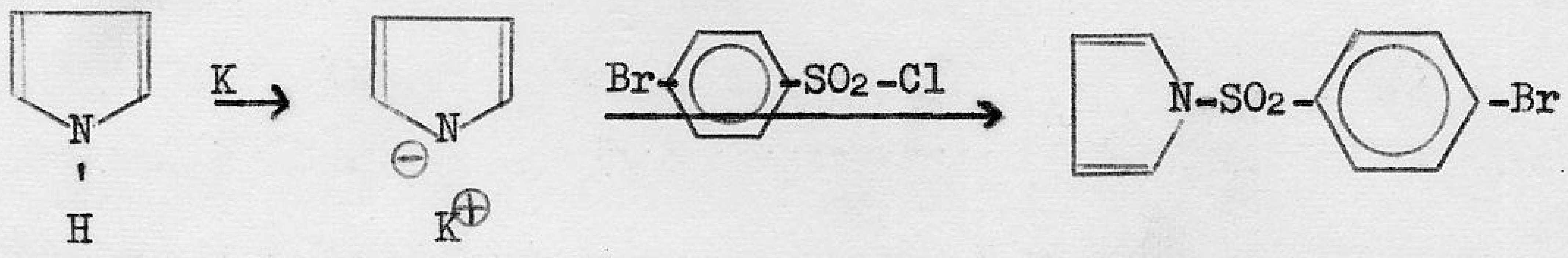
(M.p. of an analytical sample: 101.5 - 102°).

A nal. Calcd. for $C_{11}H_{11}NO_2S$: C, 59.72; H, 5.01; N, 6.33; S, 14.47.

Found: C, 59.92; H, 5.15; N, 6.31; S, 14.26.

IR Spectrum No. 2

### 3. 1-(p-Bromobenzenesulfonyl) pyrrole



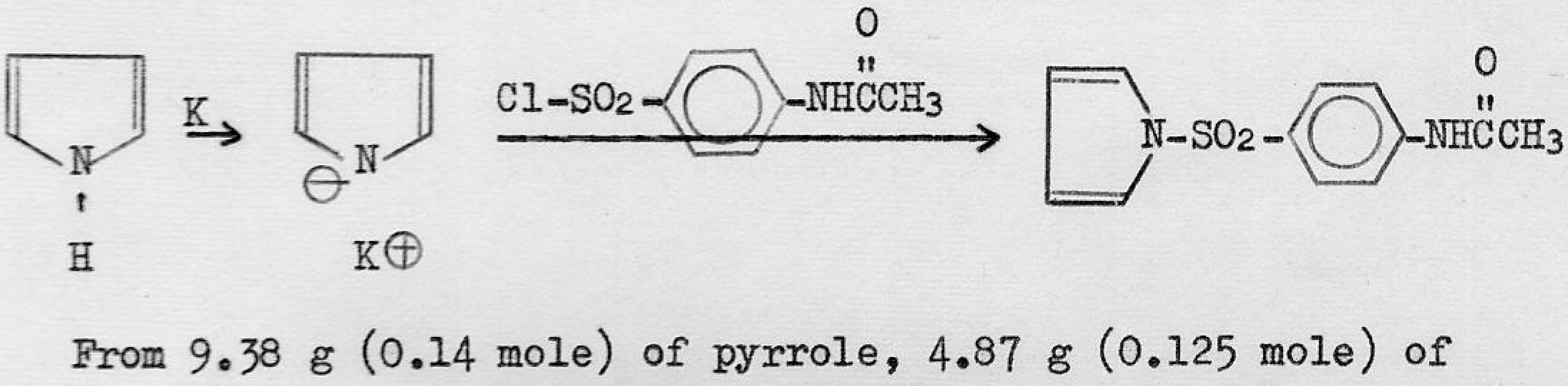
From 18.76 g (0.28 mole) of pyrrole, 9.75 g (0.25 mole) of potassium and 51.11 g (0.20 mole) of p-bromobenzenesulfonyl chloride was obtained 51.0 g (89.2%) of crude product, m.p. 130 - 133°. One recrystallization from methyl alcohol yielded white crystals melting at 133 - 134°. (M.p. of an analytical sample: 133.5 - 134°).

Anal. Calcd. for $C_{10}H_8BrNO_2S$: C, 41.97; H, 2.82; Br, 27.93; N, 4.90; S, 11.18.

Found: C, 42.02; H, 2.69; Br, 27.79; N, 4.69; S, 10.99.

IR Spectrum No. 3.

### 4. 1-(p-Acetaminobenzenesulfonyl) pyrrole



From 9.38 g (0.14 mole) of pyrrole, 4.87 g (0.125 mole) of potassium, and 23.35 g (0.10 mole) of p-acetaminobenzenesulfonyl chloride

was obtained 19.78 g (74.9%) of crude product, m.p. 148 - 150°. Two recrystallizations from methanol gave 15.7 g of material melting at 165 - 166°.

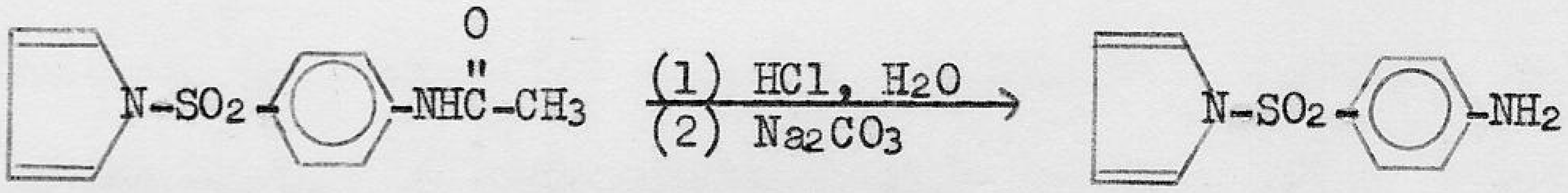
(M.p. of an analytical sample: 165.5 - 166°).

Anal. Calcd. for $C_{12}H_{12}N_2O_3S$: C, 54.54; H. 4.58; N, 10.60; S, 12.11.

Found: C, 54.61; H, 4.49; N, 10.53; S, 12.22.

IR Spectrum No. 4.

### 5. 1-(p-Aminobenzenesulfonyl) pyrrole



A mixture of 4 g of 1-(p-acetaminobenzenesulfonyl) pyrrole with 4 ml of concentrated hydrochloric acid and 4 ml of water was refluxed for 20 minutes. The product was diluted with 15 ml of water and was made alkaline to litmus by the addition of sodium carbonate. The resulting mixture was poured into 50 cc of an ice-water mixture and 3 g (89.3%) of crude product, m.p. 126 - 130°, was obtained after filtration. One recrystallization from aqueous methanol yielded 2.8 g of white crystals melting at 127 - 128°.

(M.p. of an analytical sample: 128.5 - 129°).

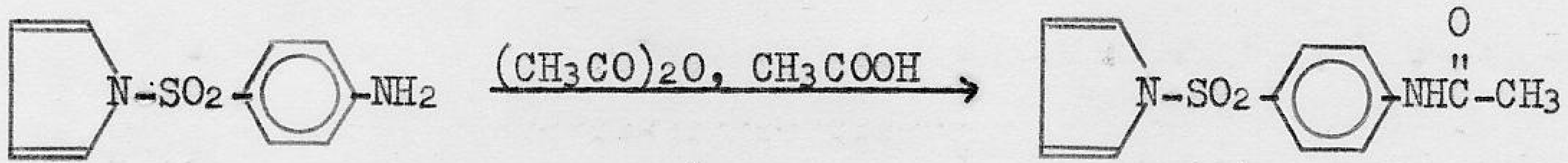
Anal. Calcd. for $C_{10}H_{10}N_2O_2S$: C, 54.05; H, 4.54; N, 12.61; S, 14.40.

Found: C, 53.87; H, 4.40; N, 12.59;

S, 14.30

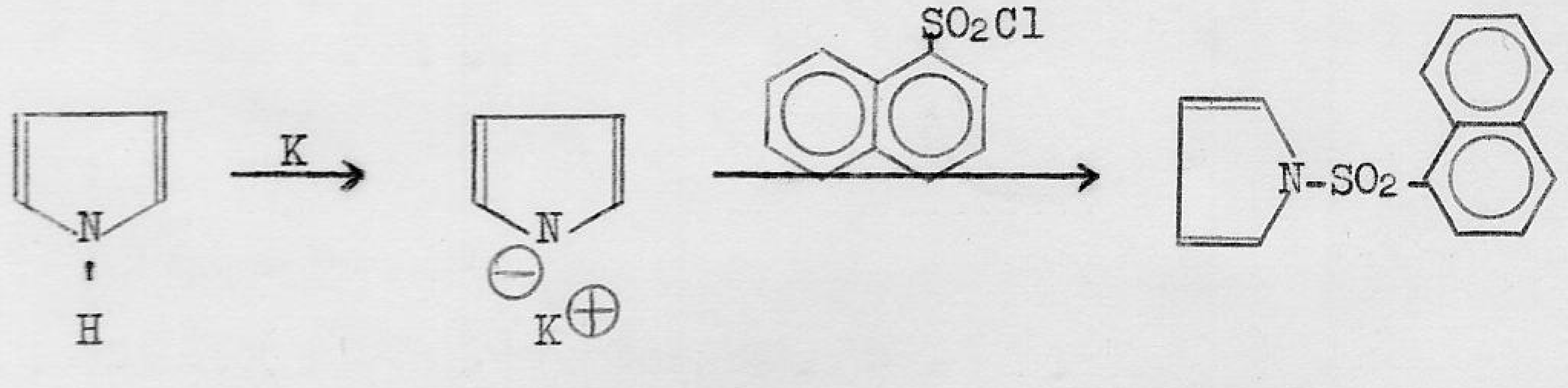
IR Spectrum No. 5

### 6. Acetylation of 1-(p-Aminobenzenesulfonyl) pyrrole



A mixture of 0.83 g of 1-(p-aminobenzenesulfonyl)pyrrole, 5 ml of glacial acetic acid, and 5 ml of acetic anhydride was refluxed for 20 minutes. After being cooled under tap water, the reaction product was poured into a beaker containing 30 g of a mixture of ice and water. Filtration afforded 0.85 g (86.2%) of crude product melting at 165 - 166°. After one recrystallization from methyl alcohol 0.72 g of material melting at 166 - 167° was recovered. A mixture melting point of the product of this reaction and 1-(p-acetaminobenzenesulfonyl) pyrrole was 166°. The identity of the product was further established by the comparison of its infrared spectrum with that of 1-(p-acetaminobenzenesulfonyl) pyrrole.

### 7. 1-(α-Naphthalenesulfonyl) pyrrole



Use of 9.38 g (0.14 mole) of pyrrole, 4.87 g (0.125 mole) of potassium, and 24.92 g (0.11 mole) of α-naphthalenesulfonyl chloride led to 22.88 g (80.9%) of crude product, m.p. 127 - 129°. One recrystallization from methyl alcohol yielded 21.9 g of white crystals melting at 131 - 132°.

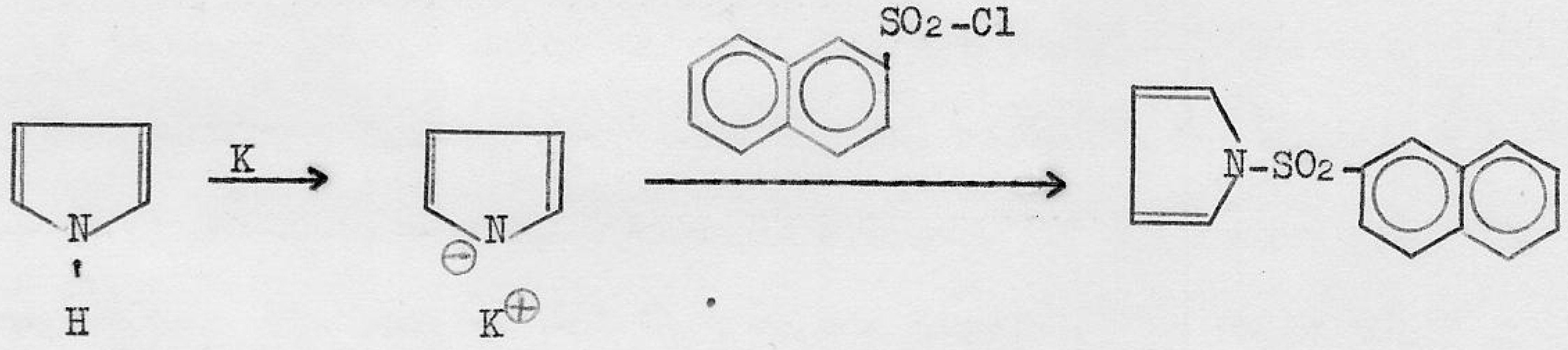
(M.p. of an analytical sample: 131.5 - 132°).

Anal. Calcd. for $C_{14}H_{11}NO_2S$: C, 65.36; H, 4.31; N, 5.45; S, 12.44.

Found: C, 65.17; H, 4.22; N, 5.36; S, 12.38.

IR Spectrum No. 6.

### 8. 1-(β-Naphthalenesulfonyl) pyrrole



With use of the same amounts of materials as in the immediately preceding reaction, the yield of crude product was 23.17 g (81.9%), m.p. 124 - 126°. After one recrystallization from methyl alcohol 21.1 g of white crystals melting at 128 - 129° was obtained.

(M.p. of an analytical sample: 127.5 - 128.5°).

Anal. Calcd. for $C_{14}H_{11}NO_2S$: C, 65.36; H, 4.31; N, 4.45; S, 12.44.

Found: C, 65.53; H, 4.21; N, 5.64; S, 12.24.

IR Spectrum No. 7

### 9. Attempted Preparation of 1-(o-nitrobenzenesulfonyl) pyrrole

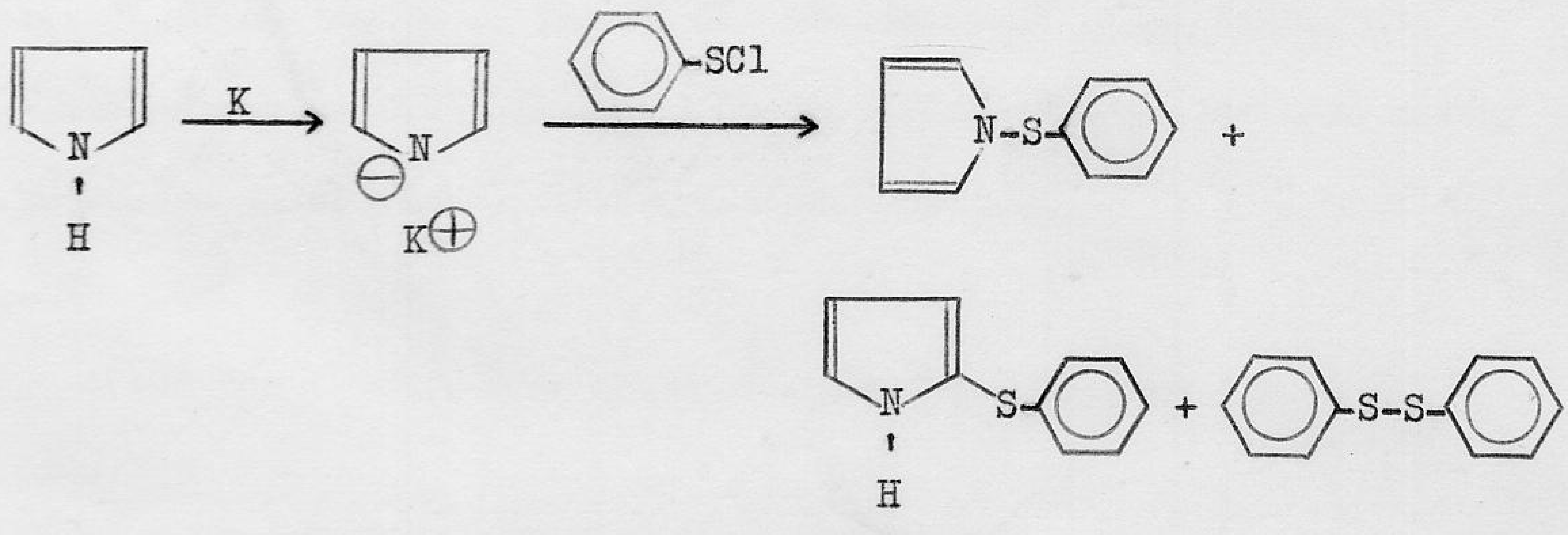
The reaction led to an intractable black tar.

All subsequent reactions, except oxidations, leading to arenesulfenyl- and arenesulfonylpyrroles were carried out in a nitrogen atmosphere.

### 10. Benzenesulfenyl chloride[39]

To an ice-cooled, stirred solution of 47.5 g of dry chlorine in 500 ml of dry carbon tetrachloride, was added dropwise over a period of one hour 30.73 g of thiophenol dissolved in 100 ml of carbon tetrachloride. After the addition was complete, the mixture was stirred for a further half hour and the carbon tetrachloride was removed by distillation under reduced pressure at the lowest possible temperature. The residue was then vacuum distilled to yield 36.90 g of benzenesulfenyl chloride, b.p. 41° / 0.25 mm; 46° / 0.30 mm. (Reported b.p. 58 - 60° / 3 mm).[40]

### 11. 1-Benzenesulfenylpyrrole and 2-benzenesulfenylpyrrole



1st Run

To a solution of 18.76 g (0.28 mole) of pyrrole in 100 ml of dry tetrahydrofuran was added a total of 9.75 g (0.25 mole) of potassium, freshly cut into small pieces under kerosene and rinsed with tetrahydrofuran. The mixture was stirred and refluxed until all the potassium reacted. Heating was then stopped, 100 ml of dry tetrahydrofuran was added, and the reaction flask was cooled for 15 minutes in a mixture of dry ice and acetone. Then 28.90 g (0.20 mole) of benzenesulfenyl chloride dissolved in 100 ml of dry tetrahydrofuran was added dropwise over a period of one hour. During this time the temperature of the reaction mixture was between -45° and -55°. After the mixture had been kept at -65° for a further four hours, it was left to stir for a period of 16 hours at room temperature. It was then filtered through a sintered glass funnel and the solid was washed with dry ether. The combined filtrate and washings were evaporated at the aspirator and the residue was fractionated in vacuum.

The following fractions were collected: 7 g (20% of the theoretical yield; 41.4% of the total yield) of 1-benzenesulfenylpyrrole, b.p. 83 - 85° / 0.16 - 0.20 mm, 6.12 g (17.5% of the theoretical yield; 36.2% of the total yield) of 2-benzenesulfenylpyrrole, b.p. 90 - 110° / 0.15 - 0.25 mm, and 3.8 g (17.4% of the theoretical yield; 22.5% of the total yield) of phenyl disulfide, b.p. 110° / 0.25 mm, m.p. 56 - 57°.

After two further fractionations the boiling points were as follows:

1-benzenesulfenylpyrrole: 80° / 0.55 mm.

2-benzenesulfenylpyrrole: 106 - 108° / 0.4 mm.

After one recrystallization of the phenyl disulfide from ethyl alcohol the m.p. became 57 - 58°. Its structure was confirmed by comparison of its infrared spectrum with that of an independently prepared sample of phenyl disulfide, the lack of depression on mixed m.p. determination (m.p. 60 - 61°) and the absence of nitrogen on elementary analysis.

Anal. Calcd. for $C_{10}H_9NS$ (1-benzenesulfenylpyrrole): C, 68.56;
H, 5.18; N, 8.00; S, 18.27.
Found: C, 68.66;
H, 5.13; N, 8.13; S, 18.16.

IR Spectrum No. 8.

Anal. Calcd. for $C_{10}H_9NS$ (2-benzenesulfenylpyrrole): C, 68.56;
H, 5.18; N, 8.00; S, 18.27.
Found: C, 68.65;
H, 5.37; N, 7.87; S, 18.42.

IR Spectrum No. 9.

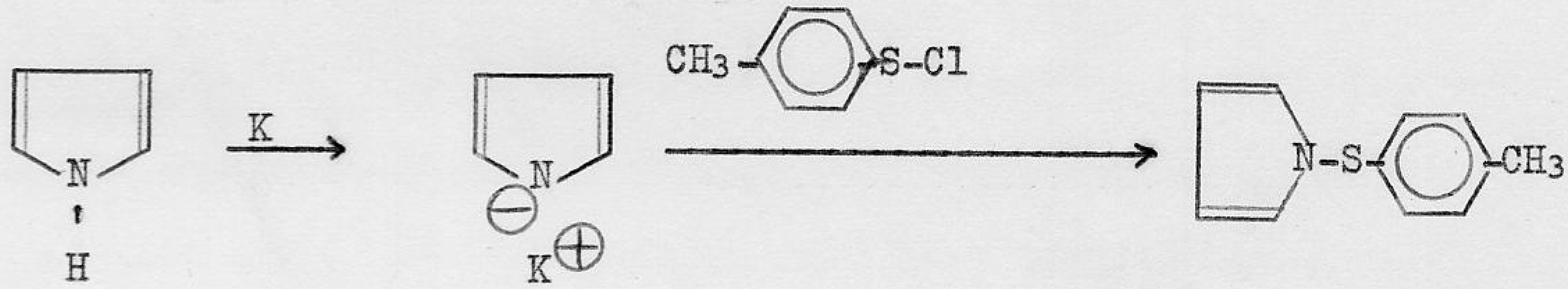
## 2nd Run

With use of the same procedure as above, from 9.38 g (0.14 mole) of pyrrole, 4.87 g (0.125 mole) of potassium, and 14.45 g (0.1 mole) of the benzenesulfenyl chloride was obtained 4.0 g (22.9% of the theoretical yield; 44.0% of the total yield) of 1-benzenesulfenylpyrrole, b.p. 79 - 82° / 0.18 mm, 3.1 g (17.7% of the theoretical yield; 34.1% of the total yield) of 2-benzenesulfenylpyrrole, b.p. 98 - 105° / 0.18 mm, and 2 g (18.3% of the theoretical yield; 22.0% of the total yield) of phenyl disulfide, b.p. 105° / 0.18 mm.

### 12. p-Toluenesulfenyl chloride[39]

To an ice-cooled, stirred solution of 75 g of dry chlorine in 750 ml of dry carbon tetrachloride, was added dropwise, over a period of one hour, 54.6 g of p-toluenethiol in 150 ml of dry carbon tetrachloride. After the addition was complete the mixture was stirred for a further half hour and the carbon tetrachloride was removed by distillation at reduced pressure at the lowest possible temperature. Distillation of the residue in vacuum yielded 44.9 g of p-toluenesulfenyl chloride, b.p. 80 - 82° / 2.4 - 2.5 mm, $n^{18^\circ} = 1.6067$. (Reported b.p. 66 - 68° / 0.8 mm; 74-76° / 1.5 mm; 82 - 84° / 3.5 mm; $n^{20^\circ} = 1.6018 - 1.6019$).

### 13. 1-(p-Toluenesulfenyl) pyrrole



The procedure was the same as for the preparation of 1- and 2-bezenesulfenylpyrrole, except that the reaction was run at room temperature, in ice and salt, and in dry ice and acetone.

### Reaction run at room temperature

From 9.38 g (0.14 mole) of pyrrole, 4.87 g (0.125 mole) of potassium and 15.85 g (0.10 mole) of p-toluenesulfenyl chloride was obtained 4.60 g (24.3% of the theoretical yield; 51.9% of the total yield) of 1-(p-toluenesulfenyl) pyrrole as a low melting solid, b.p. 105 - 115° / 0.4 - 0.5 mm, and 4.27 g of a yellow oil, b.p. 155 -

170° / 0.4 - 0.5 mm, which solidified on standing at room temperature.

Reaction run in ice and salt

The same amounts of reagents as above yielded 6.19 g (32.8% of the theoretical yield; 72.6% of the total yield) of 1-(p-toluenesulfenyl) pyrrole, b.p. 109 - 112° / 0.20 - 0.25 mm, and 2.33 g of a yellow oil, b.p. 150 - 162° / 0.15 - 0.275 mm, which solidified on standing at room temperature.

The first fractions of the two runs were combined (10.79 g) and fractionated again giving 8.53 g of liquid, b.p. 94 - 96° / 0.58 - 0.60 mm. A third fractionation gave white crystals of 1-(p-toluenesulfenyl) pyrrole boiling at 83 - 85° / 0.05 mm.

Anal. Calcd. for $C_{11}H_{11}NS$, 1-(p-toluenesulfenyl) pyrrole:

C, 69.82; H, 5.86; N, 7.40; S, 16.91.

Found: C, 69.55; H, 5.98; N, 7.42; S, 16.79.

IR Spectrum No. 10.

The second fractions of the two runs were combined (6.60 g) and fractionated again, but the boiling point rose continuously from 141° to 174° / 0.25 - 0.50 mm, and no distinct fractions could be collected. On a third fractionation, the yellow oil distilled again continuously at 132° - 153° / 0.9 - 1.05 mm , three fractions were, however, collected:

Fraction 1, b.p. 132° - 139° / 0.9 - 1.0 mm.

Fraction 2, b.p. 134° - 147° / 0.75 mm.

Fraction 3, b.p. 151° - 153° / 0.80 - 1.0 mm.

The third fraction was analyzed for C, H, N, S but the results did not fit any reasonable formula.

Reaction run in dry ice and acetone

From 13.40 g (0.20 mole) of pyrrole, 6.83 g (0.175 mole) of potassium, and 23.78 g (0.15 mole) of p-toluenesulfenyl chloride was obtained 4 g (14.1% of the theoretical yield; 27.2% of the total yield) of 1-(p-toluenesulfenyl) pyrrole, b.p. 88 - 90° / 0.4 mm, and 10.70 g of a yellow oil, b.p. 98 - 147° / 0.35 mm, which solidified at room temperature.

Upon refractionation of the 2nd fraction, material distilling between 120 - 130° / 0.15 mm was collected which on further distillation boiled at 116 - 120° / 0.10 - 0.15 mm. This last distillate, a solid at room temperature, was recrystallized from absolute ethyl alcohol to give white needles melting at 45°. Elementary analysis showed absence of nitrogen; the lack of any depression on mixed melting determination with p-tolyl disulfide (m.p. 45°) and the identical infrared spectra showed that the solid was p-tolyl disulfide.

14. Reaction of pyrrolylmagnesium bromide with benzenesulfenyl chloride

A solution of 16.35 g (0.15 mole) of ethyl bromide in 50 ml of dry ether was added dropwise, with stirring, over a period of half an hour to 3.04 g (0.125 mole) of magnesium turnings covered with 50 ml of dry ether. After the resulting mixture had been refluxed for approximately half an hour, a solution of 7.54 g (0.125 mole) of pyrrole in 50 ml of dry ether was added dropwise over a period of half an hour. Cooling of the mixture in ice and salt, and dilution with 50 ml of dry ether was followed by the dropwise addition of 14.45 g (0.10 mole) of benzenesulfenyl chloride dissolved in 50 ml of dry ether over a period of half an hour. After the mixture had been stirred for 16 hours, it was hydrolyzed by the slow addition of a solution of 13.40 g (0.25 mole) of ammonium chloride in 150 ml of water. Vigorous stirring for half an hour was followed by filtration and separation of the layers in the filtrate. The combined organic layer and ether washings of the aqueous layer were dried over anhydrous magnesium sulfate and evaporated at the aspirator. Vacuum distillation of the residue gave only 2.52 g (14.4%) of a yellow oil boiling between 124 and 133° / 0.35 - 0.50 mm, which upon a second distillation distilled at 115 - 126° / 0.450 - 0.650 mm.

Thin layer chromatography of the product on silica gel with chloroform as the solvent showed 3 spots, indicating that the distillate was a mixture of at least 3 compounds.

IR Spectrum No. 12.

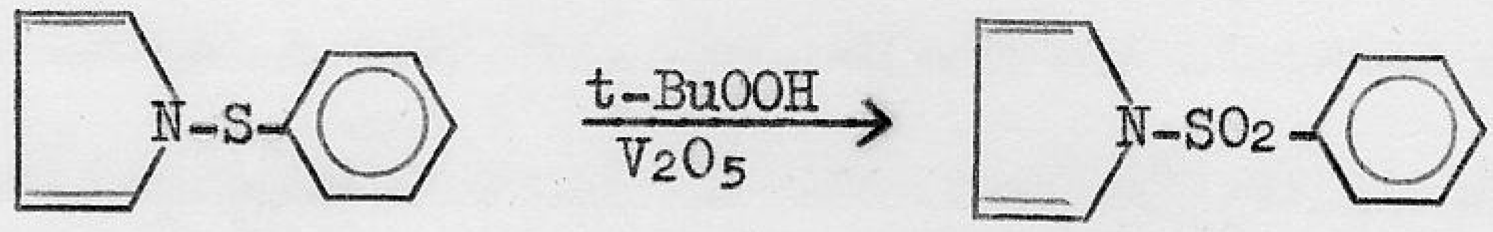
15. Reaction of pyrrolylmagnesium bromide with p-toluenesulfenyl chloride

The same procedure and quantities of reagents as in the previously described reaction with benzenesulfenyl chloride led to the isolation of 3.7 g (19.6%) of an oil, b.p. 130 - 140° / 0.25 - 0.50 mm.

Thin layer chromatography on silica gel with chloroform as the solvent showed 3 spots, indicating that the distillate was a mixture of at least 3 compounds.

IR Spectrum No. 13.

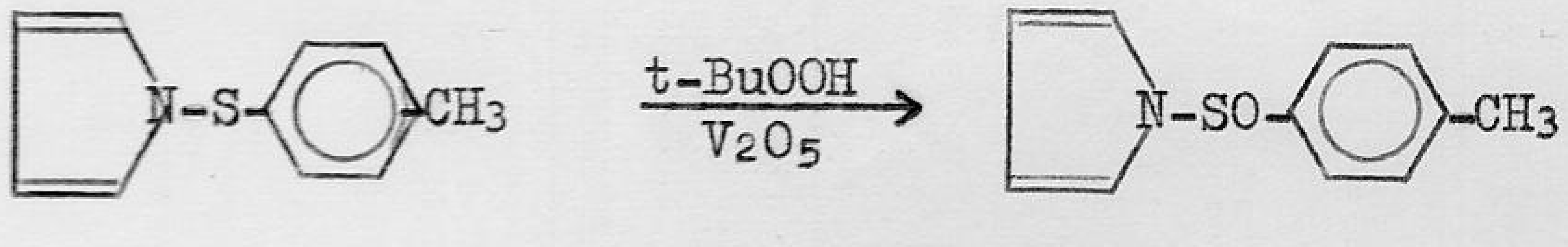
### 16. Oxidation of 1-benzenesulfenylpyrrole to 1-benzenesulfonylpyrrole



To a solution of 1 g of 1-benzenesulfenylpyrrole in 5 ml of absolute ethyl alcohol, 1 g of a 75% solution of tert-butyl hydroperoxide in tert-butyl peroxide was slowly added and the mixture was boiled for 15 seconds. A small amount of Vanadium pentoxide was then added and the mixture was left to stand for 2 hours at room temperature. It was then filtered and the filtrate was brought to the top of a neutral alumina column and was eluted with ether. The ether solution was evaporated and the thick brown oil obtained was left to stand at room temperature for 2 days, after which 0.12 g of transparent crystals melting at 78 - 81° was collected by filtration. Recrystallization from methyl alcohol yielded 0.10 g (8.5%) of 1-benzenesulfonylpyrrole melting at 85 - 86°.

The product was identified by comparison of its infrared spectrum with that of an authentic sample of 1-benzenesulfonylpyrrole. There was no melting point depression on mixing the two samples (m.p. 84.5 - 85.5°).

### 17. Oxidation of 1-(p-toluenesulfenyl)pyrrole to 1-(p-toluenesulfinyl) pyrrole



To 1 g of 1-(p-toluenesulfenyl) pyrrole dissolved in 5 ml of absolute ethyl alcohol was slowly added 1 g of a 75% solution of tert-butyl hydroperoxide in tert-butyl peroxide and the mixture was boiled for 15 seconds. After the addition of a small amount of vanadium pentoxide the mixture was left to stand at room temperature for an hour, by which time a white crystalline solid had been formed. The crystals were collected by filtration and recrystallized from absolute ethyl alcohol giving 0.68 g (63%) of 1-(p-toluenesulfinyl) pyrrole melting at 90 - 91°.

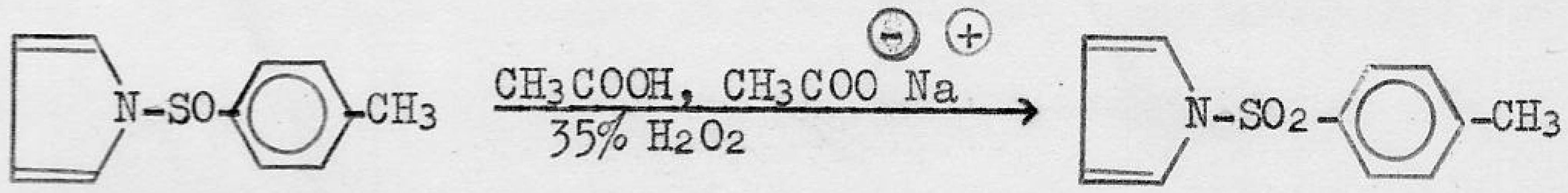
(Melting point of an analytical sample: 92.5°)

IR Spectrum No. 11

Anal. Calcd. for $C_{11}H_{11}NOS$: C, 64.38; H, 5.40; N, 6.83; S, 15.59.

Found: C, 64.21; H, 5.37; N, 6.68; S, 15.57.

18. Oxidation of 1-(p-toluenesulfinyl) pyrrole to 1-(p-toluenesulfonyl) pyrrole



To 0.34 g of 1-(p-toluenesulfinyl) pyrrole was added 0.49 g of sodium acetate, 2 ml of glacial acetic acid and 4 ml of 35% hydrogen peroxide. After the mixture had been stirred for 24 hours with a magnetic stirrer, it was diluted with 20 ml of water and filtered to yield 0.22 g (60%) of 1-(p-toluenesulfonyl) pyrrole, m.p. 100 - 101°.

The product was identified by comparison of its infrared spectrum with that of an authentic sample of 1-(p-toluenesulfonyl) pyrrole.

There was no melting point depression on mixing the two samples, (m.p. 100 - 101°).

Attempted oxidation of 1-(p-toluenesulfinyl) pyrrole with tert-butyl hydroperoxide and vanadium pentoxide gave only traces of the 1-(p-toluenesulfonyl) pyrrole.

### 19. Attempted reaction of pyrrolylpotassium with 2,4-dinitrobenzenesulfenyl chloride

To a solution of 9.38 g (0.14 mole) of pyrrole in 50 ml of dry tetrahydrofuran was added 4.87 g (0.125 mole) of potassium, freshly cut into small pieces and rinsed with tetrahydrofuran. The mixture was stirred and refluxed until all the potassium had reacted. Following the addition of 50 ml of tetrahydrofuran, the reaction mixture was cooled in ice and salt and 23.45 g (0.10 mole) of 2,4-dinitrobenzenesulfenyl chloride dissolved in 75 mls of tetrahydrofuran was added dropwise over a period of one hour. The mixture was stirred for 16 hours, filtered, and the solid material was washed with dry ether. The combined filtrate and ether washings were evaporated at the aspirator to yield a black, thick tar which decomposed into a black solid mass upon an attempt at distillation in vacuum.

### 20. Attempted reaction of pyrrolylsodium with 2,4-dinitrobenzenesulfenyl chloride

To 5.5 g (0.125 mole) of 54.2% sodium hydride in 50 ml of dry tetrahydrofuran, was added 9.38 g (0.14 mole) of pyrrole dissolved in 50 ml of tetrahydrofuran, dropwise over a period of half an hour.

When the addition was complete, the mixture was refluxed for 15 minutes and the resulting solution of pyrrolylsodium was added dropwise over a period of one hour to a cooled solution of 23.45 g (0.10 mole) of 2,4-dinitrobenzenesulfenyl chloride in 50 ml of tetrahydrofuran. The temperature of the mixture during the reaction was kept between -10° and -20°. The mixture was stirred for four hours and filtered. A grey solid, which was washed with dry ether, was collected. The combined filtrate and washings were evaporated at the aspirator to yield a thick balck tar which decomposed into a solid black mass upon an attempt at distillation in vacuum. The grey solid collected was identified as 2,4-dinitrobenzenesulfenyl chloride by comparison of its infrared spectrum with that of the pure reagent.

### 21. Attempted preparations of 2-arenesulfonylpyrroles

### a. The use of pyrrolylmagnesium bromide.

### i. Reaction of pyrrolylmagnesium bromide with benzenesulfonyl chloride

A solution of 32.6 g (0.30 mole) of ethyl bromide in 100 ml of dry ether was added dropwise to 6.08 g (0.25 mole) of magnesium turnings covered with 100 ml of ether, and the mixture was refluxed with stirring for approximately one hour. To the resulting solution, 15.08 g (0.225 mole) of pyrrole dissolved in 100 ml of dry ether was slowly introduced and this was followed by dilution with 100 ml of dry ether. Subsequently, a solution of 35.30 g (0.20 mole) of benzenesulfonyl chloride in 100 ml of dry ether was added dropwise over a period of one hour and the resulting mixture was stirred for

16 hours. Hydrolysis was effected by the addition of 26.75 g (0.50 mole) of ammonium chloride dissolved in 150 ml of water with cooling and stirring. Filtration yielded a black, tarry solid which was washed with ether, the ether washings being added to the filtrate. The ether layer was separated, dried over anhydrous magnesium sulfate, and evaporated at the aspirator to give a black, tarry solid similar to that collected by filtration. All attempts to decolorize or recrystallize this material failed.

ii. Inverse addition

A similar reaction in which a solution of the Grignard reagent was slowly added to a solution of the sulfonyl chloride also yielded an intractable tar.

iii. Reaction of pyrrolylmagnesium bromide with β-naphthalenesulfonyl chloride in tetrahydrofuran

The reaction led to an intractable black tar.

b. Reaction of pyrrole with benzenesulfonyl chloride in the presence of zinc chloride

To a mixture of 44.15 g (0.25 mole) of benzenesulfonyl chloride and 71.56 g (0.528 mole) of anhydrous zinc chloride, a solution of 16.75 g (0.25 mole) of pyrrole in 200 mls of dry cyclohexane was added dropwise with stirring. As there was no evolution of hydrogen chloride, the mixture was heated in an attempt to cause the reaction to start, but within about 15 minutes the contents of the reaction flask had polymerized to a solid.

c. Reaction of pyrrole with benzenesulfonyl chloride in the presence of potassium carbonate

A mixture of 33.5 g (0.5 mole) of pyrrole, 34.55 g (0.25 mole) of potassium carbonate, 88.25 g of benzenesulfonyl chloride, 100 mls of dry toluene, and 100 mls of water was stirred for 24 hours. After separation of the organic layer, the aqueous layer was washed with ether, and the combined organic layer and ether washings were dried over anhydrous magnesium sulfate. Removal of solvents at the aspirator yielded a black tarry residue.

d. Reaction of 1-(p-toluenesulfonyl) imidazole with pyrrole

1st Run

A mixture of 35.52 g (0.16 mole) of 1-(p-toluenesulfonyl) imidazole[41] with 21.44 g (0.32 mole) of pyrrole was refluxed for 5 hours in a nitrogen atmosphere. The product which consisted of a thick black tar was cooled and extracted with ether. Evaporation of the ether extracts at the aspirator yielded also a black tar. Extraction of the tar with boiling ligroin followed by evaporation led to a tarry material.

2nd Run

The same reaction was run at 60 - 70° for 4 days. The product was washed with water to remove any imidazole and then extracted with ether. Evaporation of the ether solution yielded crystals of 1-(p-toluenesulfonyl) imidazole as evidenced by inspection of the infrared spectrum and by a mixed melting point determination (77 - 78°).

e. Reaction of 1-pyrrolecarboxanilide with benzenesulfonyl chloride in the presence of boron trifluoride

A solution of 24.35 g (0.131 mole) of 1-pyrrolecarboxanilide[42] in 100 ml of tetrahydrofuran was added dropwise over a period of one hour to 23.12 g (0.131 mole) of benzenesulfonyl chloride and 18.59 g of boron trifluoride etherate in 100 ml of tetrahydrofuran. The mixture was stirred for 2 days at room temperature and for 2 hours at reflux. Removal of the solvent led to almost quantitative recovery of 1-pyrrolecarboxanilide.

f. Reaction of 1-pyrrolecarboxanilide with benzenesulfonyl chloride in the presence of aluminum chloride

To a mixture of 11.5 g (0.065 mole) of benzenesulfonyl chloride, 8.66 g (0.065 mole) of aluminum chloride, and 150 ml of carbon disulfide was added dropwise over a period of 30 minutes 12 g (0.065 mole) of 1-pyrrolecarboxanilide dissolved in 150 ml of carbon disulfide. After completion of the addition which caused an exothermic reaction to occur, the mixture was stirred for 24 hours at room temperature. Filtration yielded a solid which was washed with carbon disulfide. Evaporation of the combined filtrate and washings at the aspirator did not give any residue. All attempts to recrystallize the solid failed.

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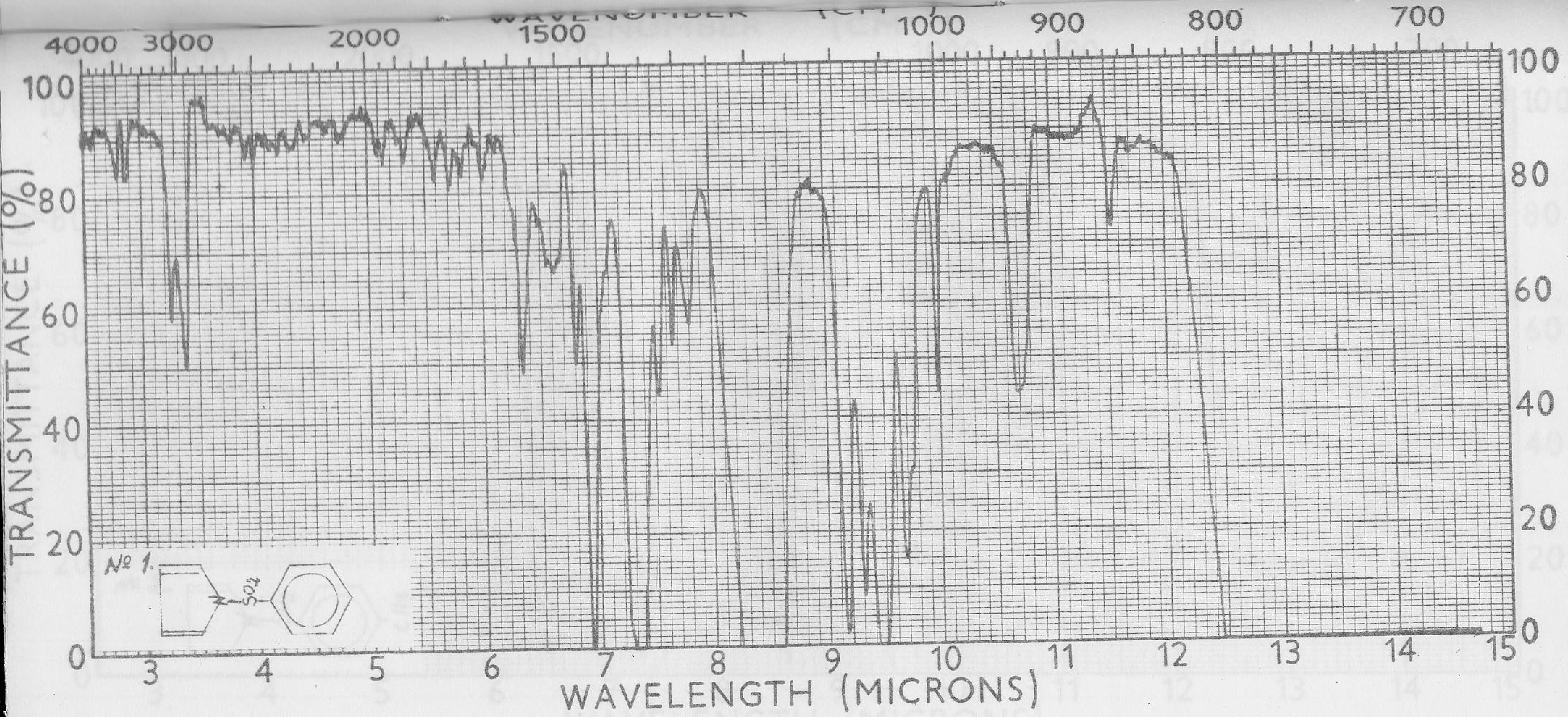
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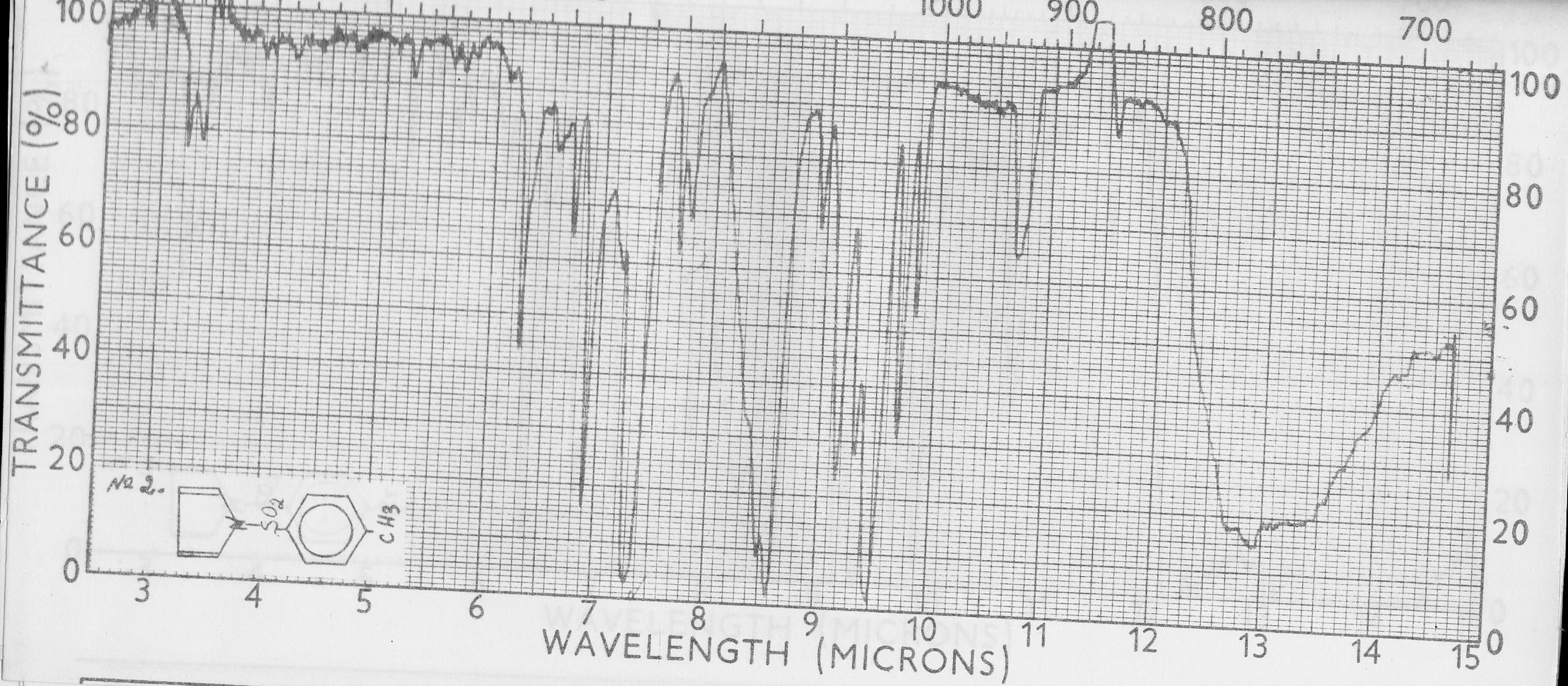
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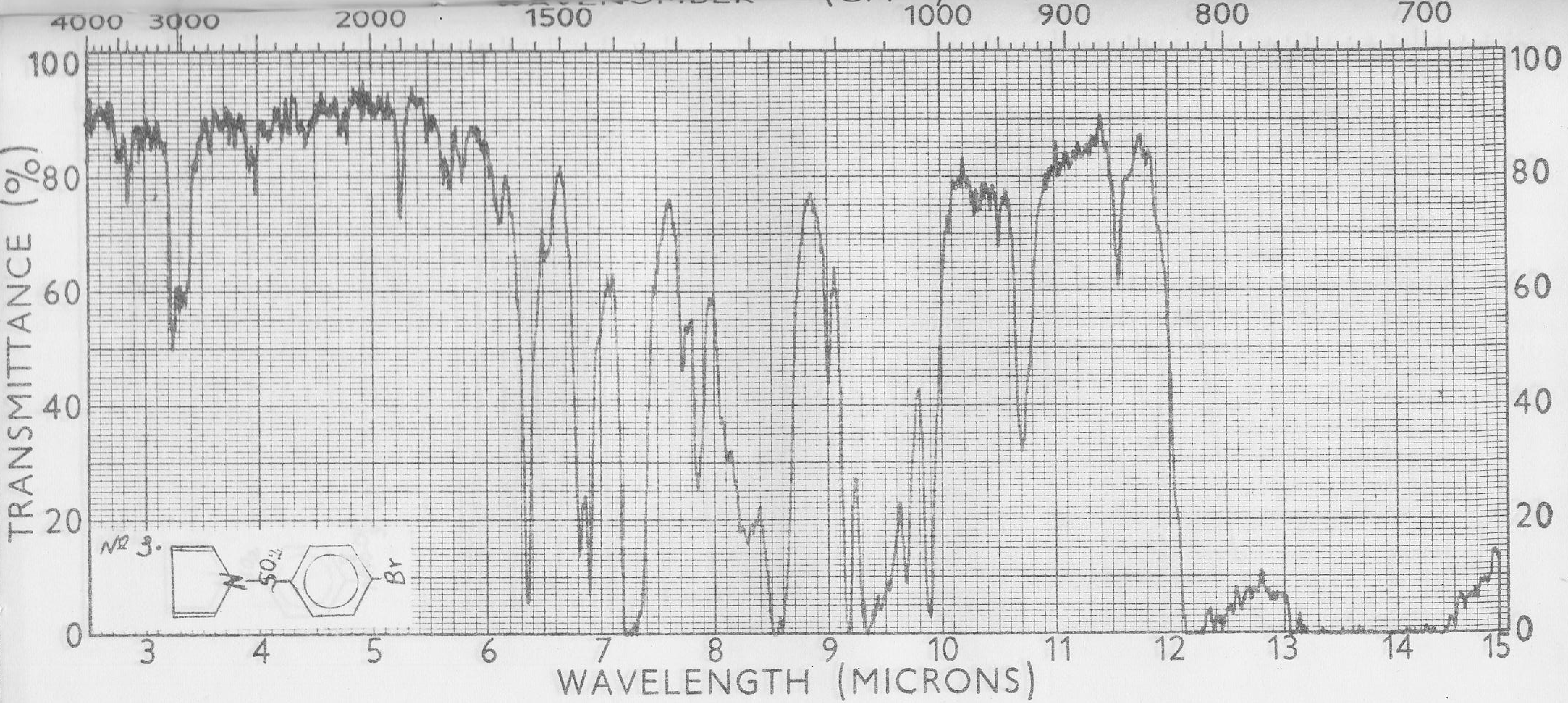
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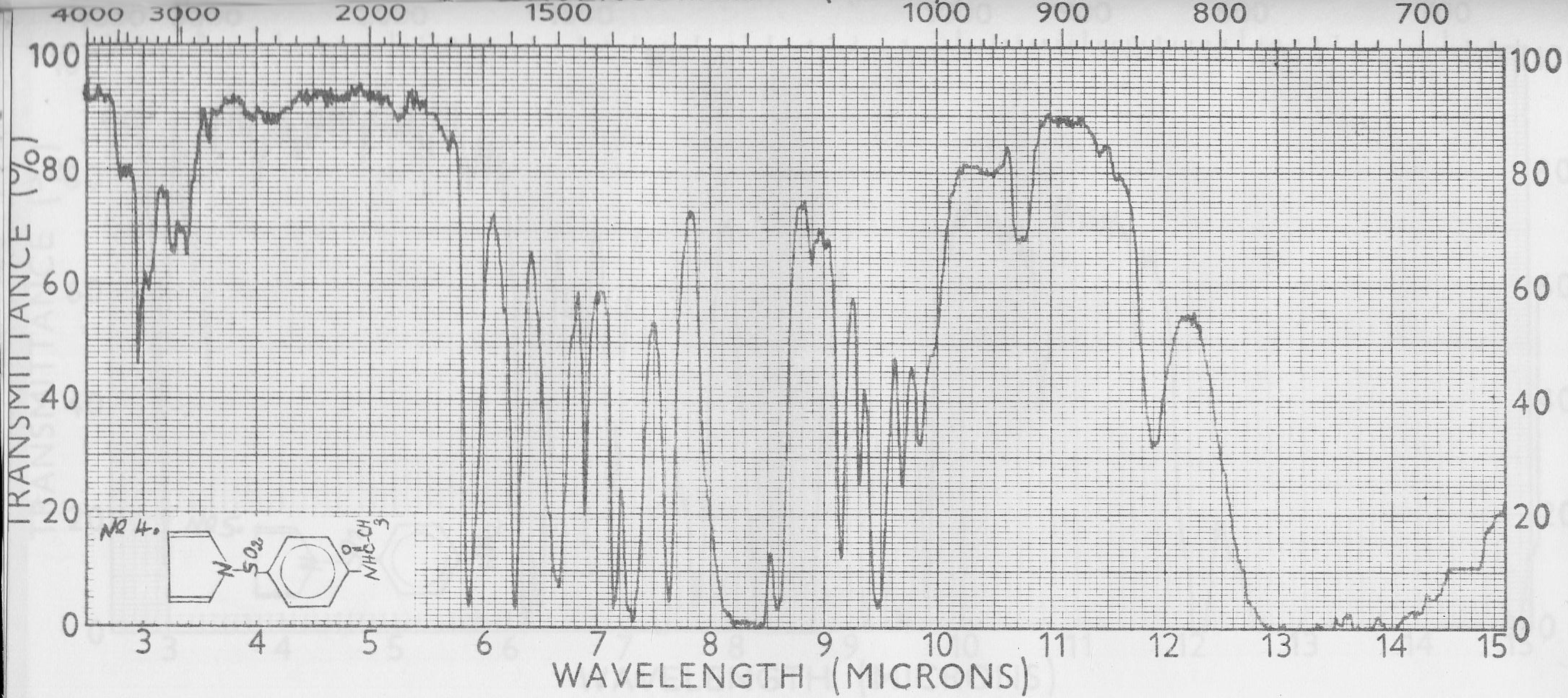
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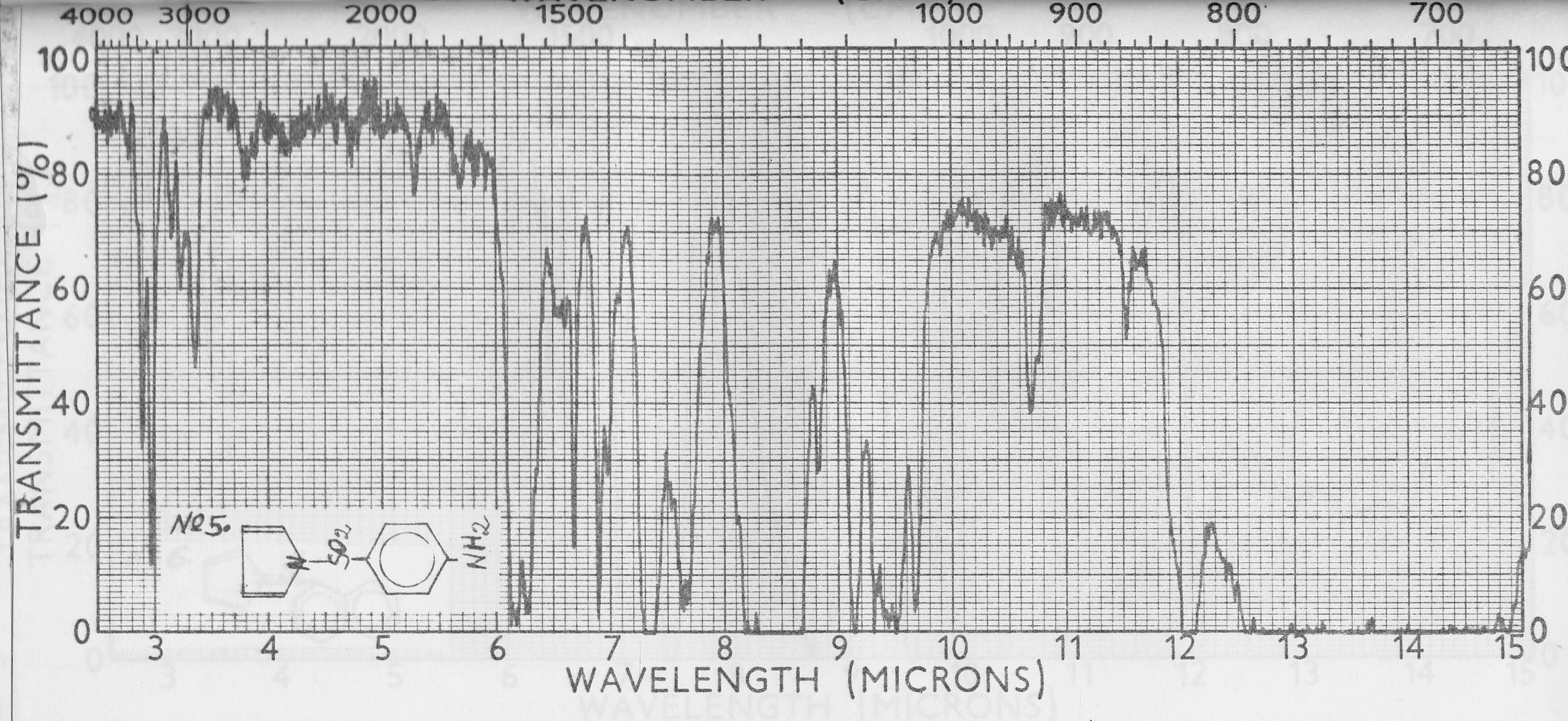
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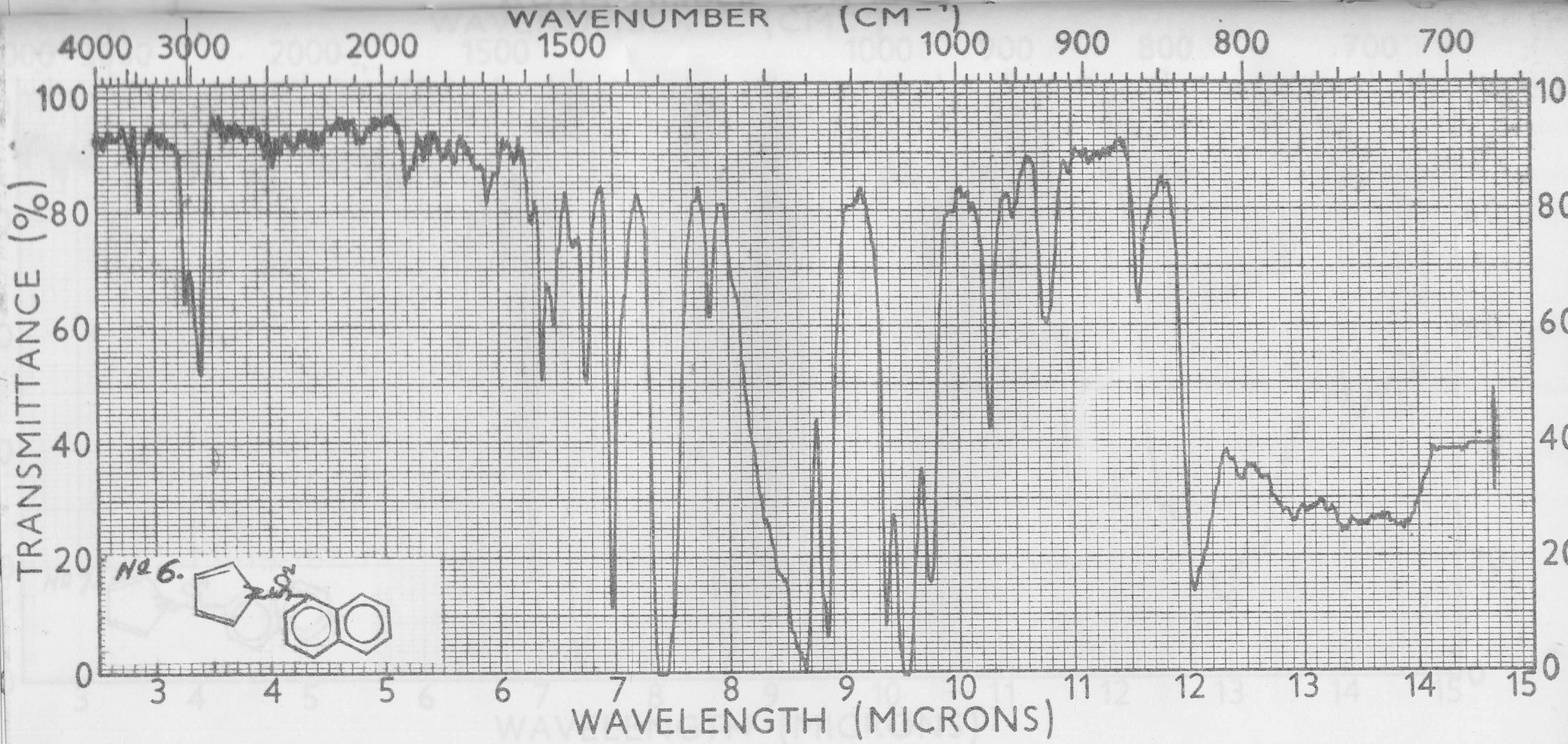
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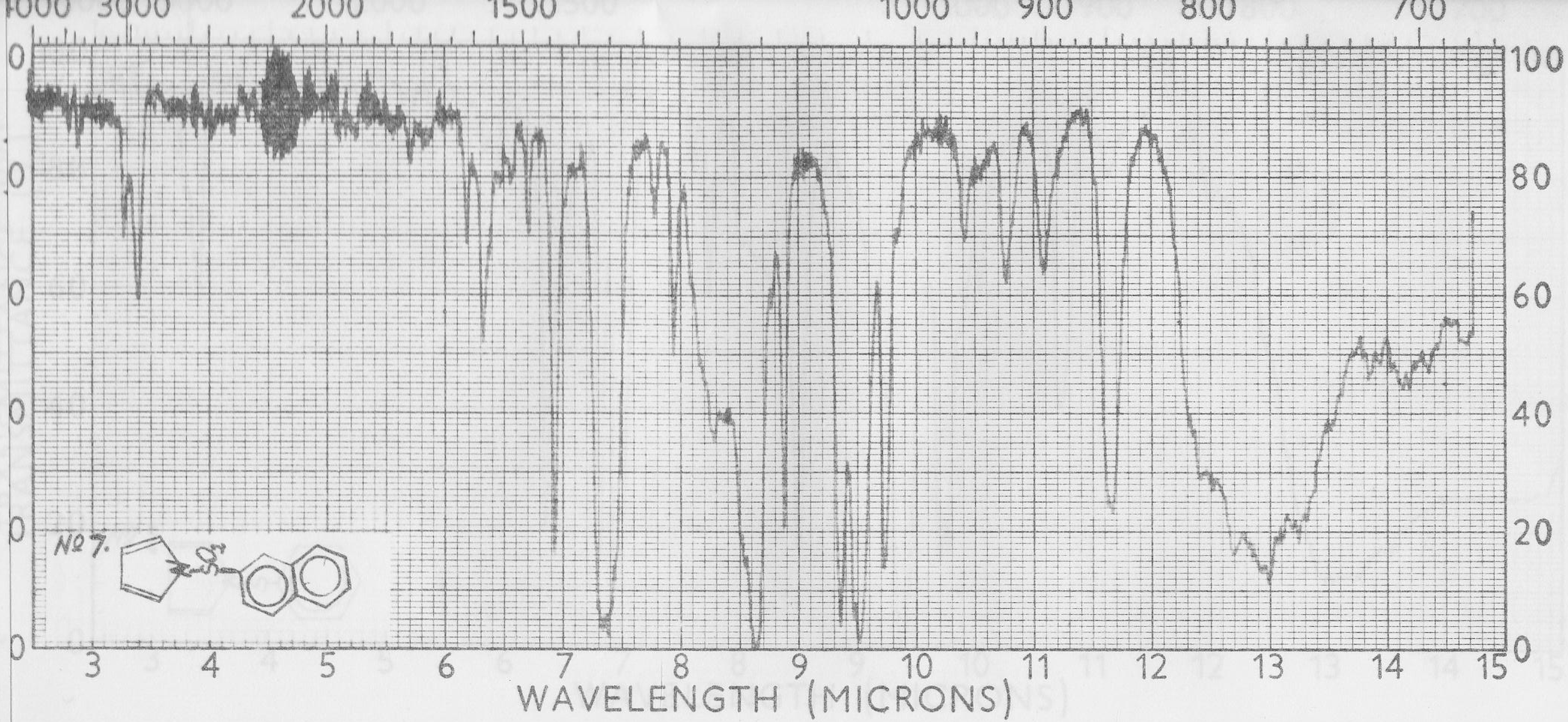

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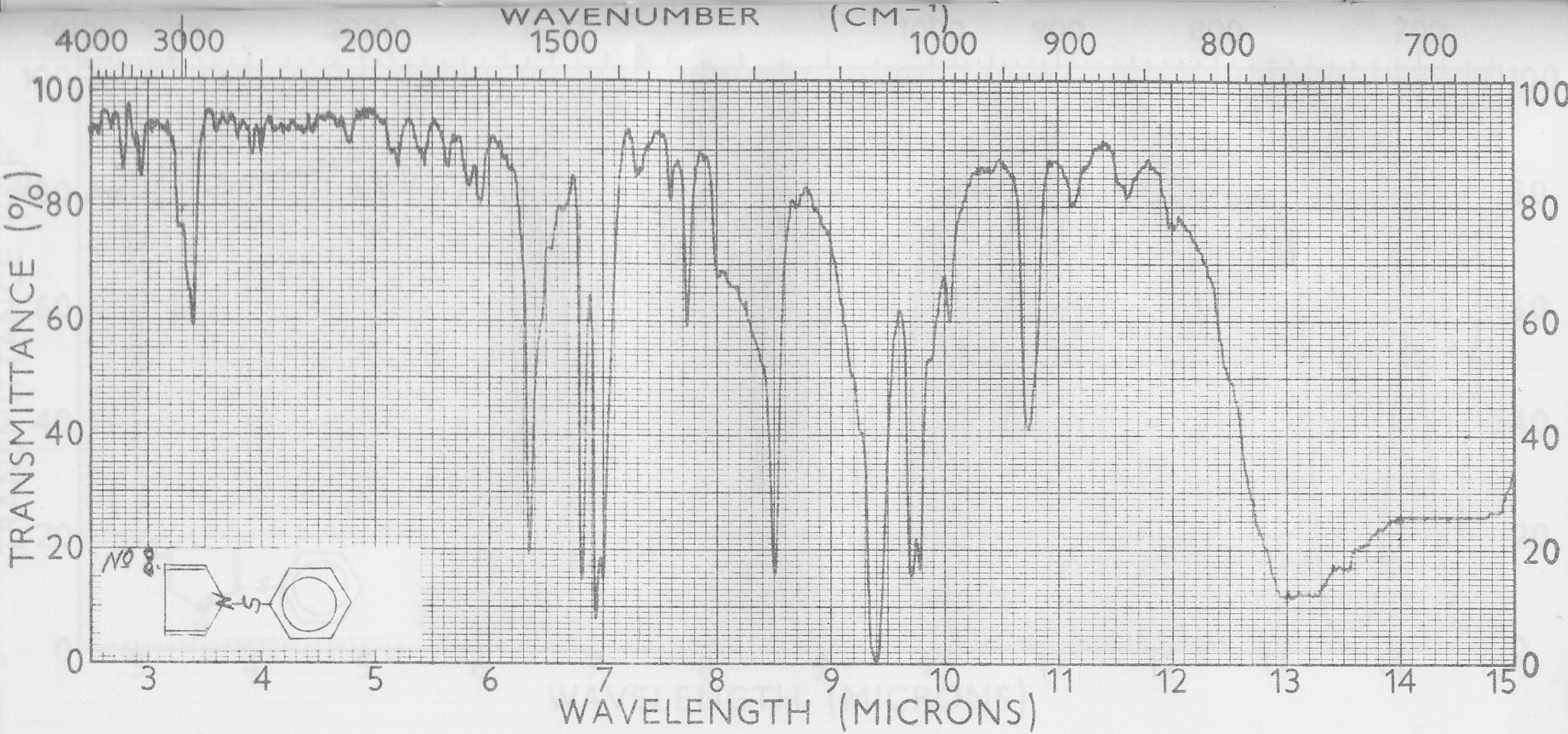
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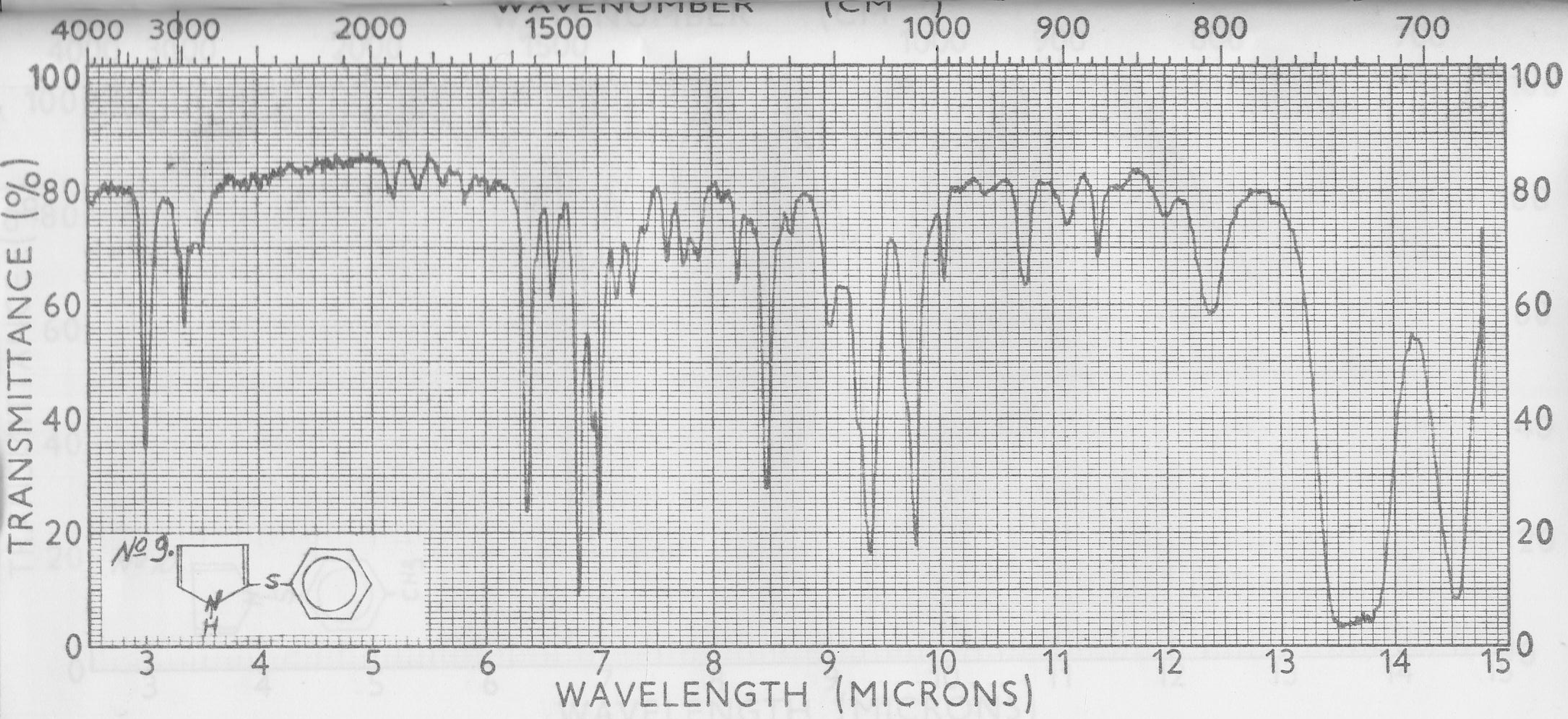WAVENUMBER (CM
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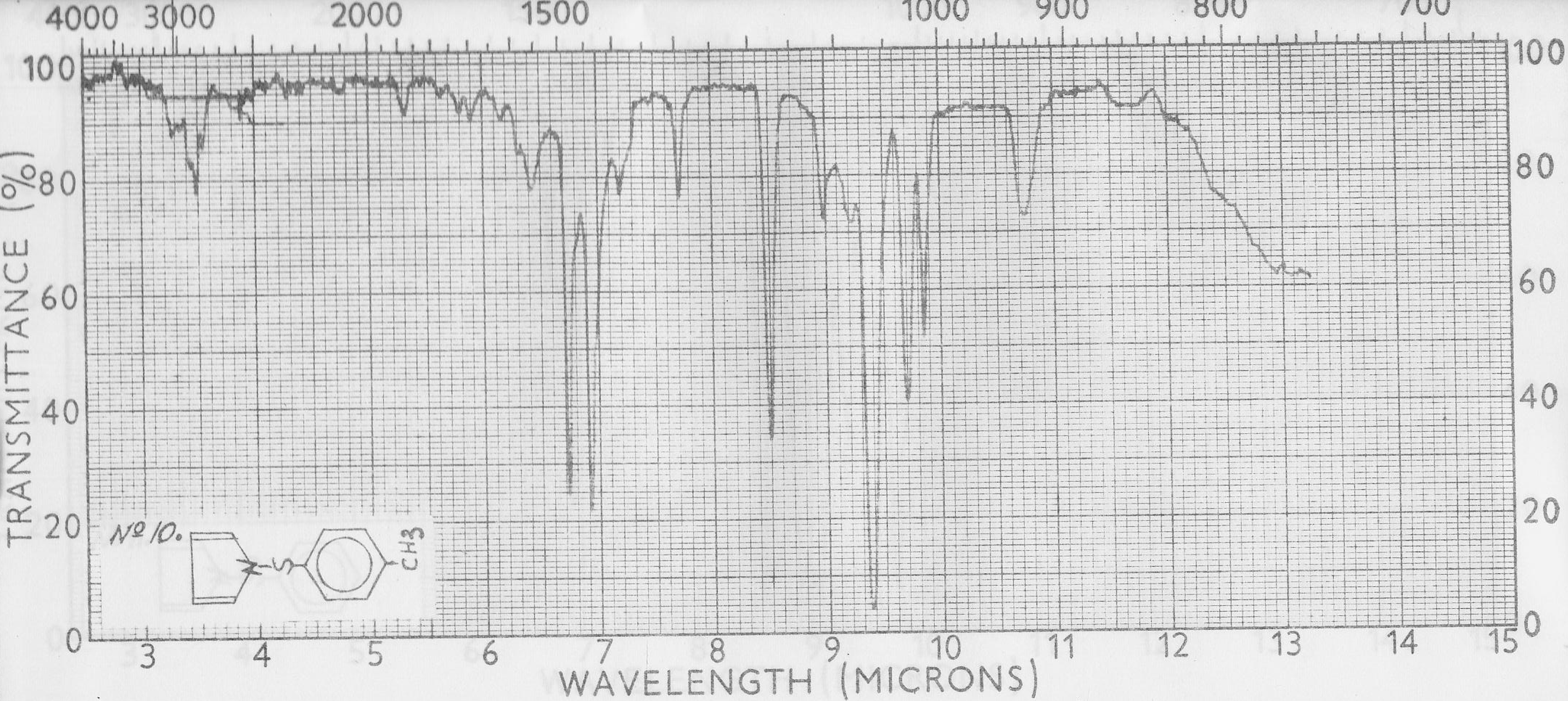
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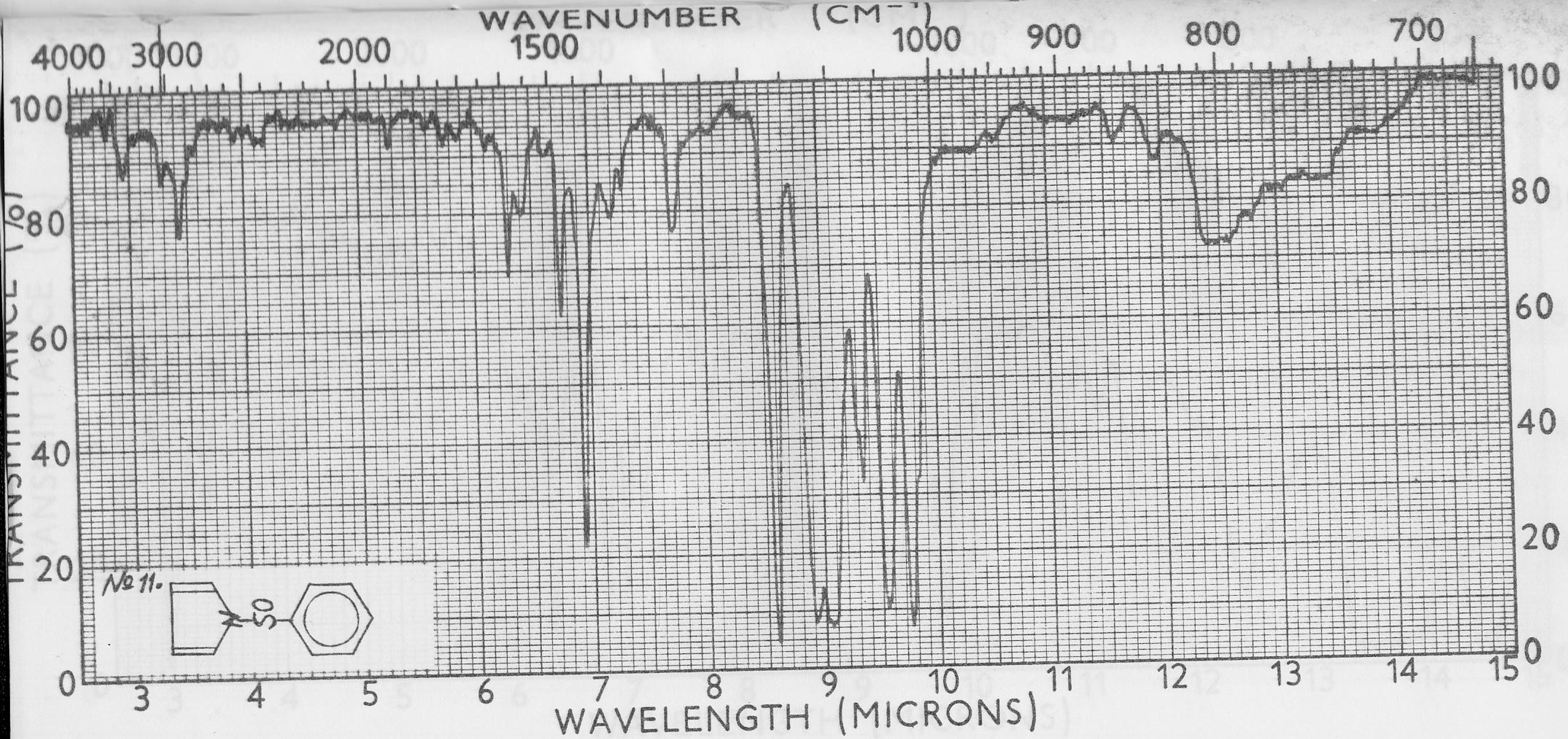
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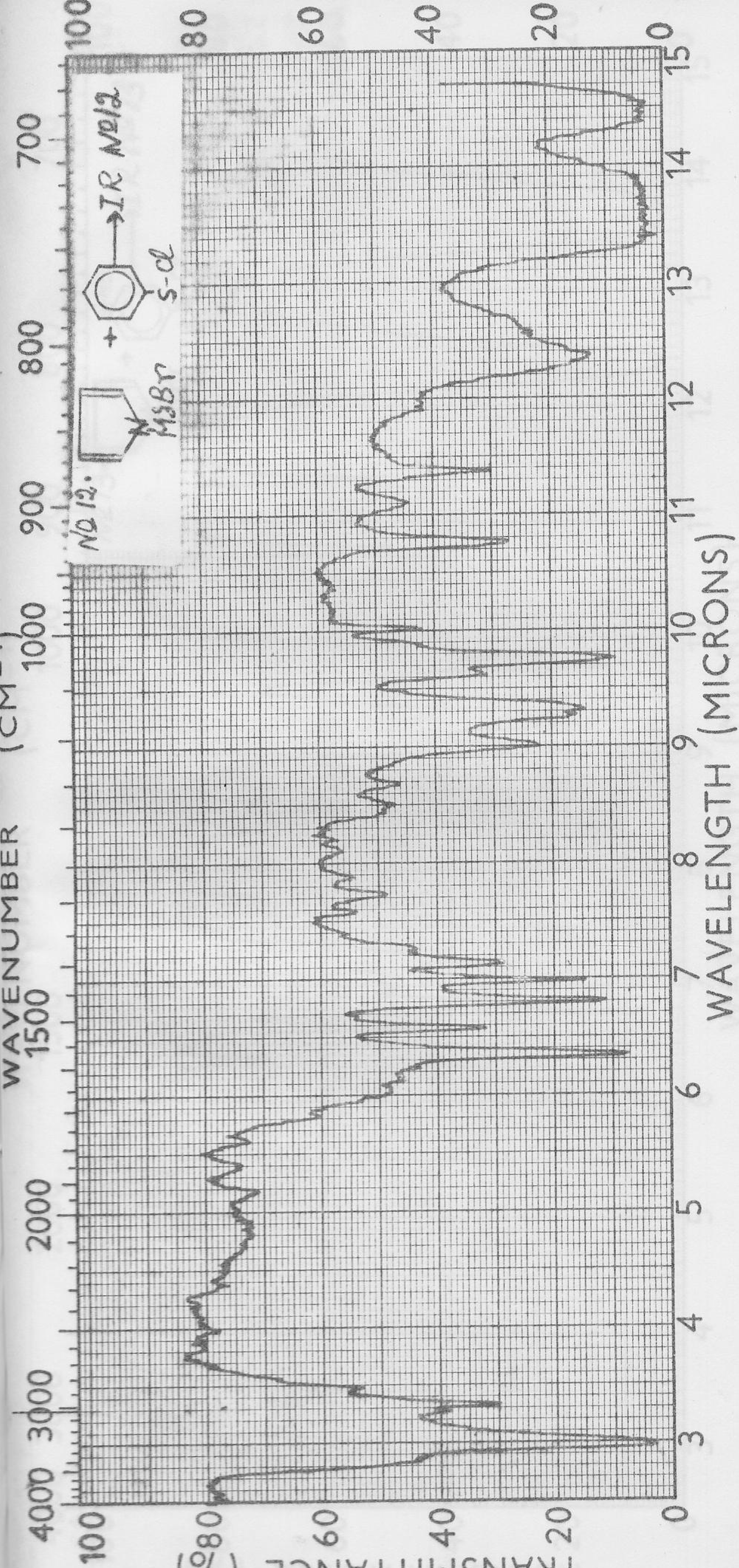
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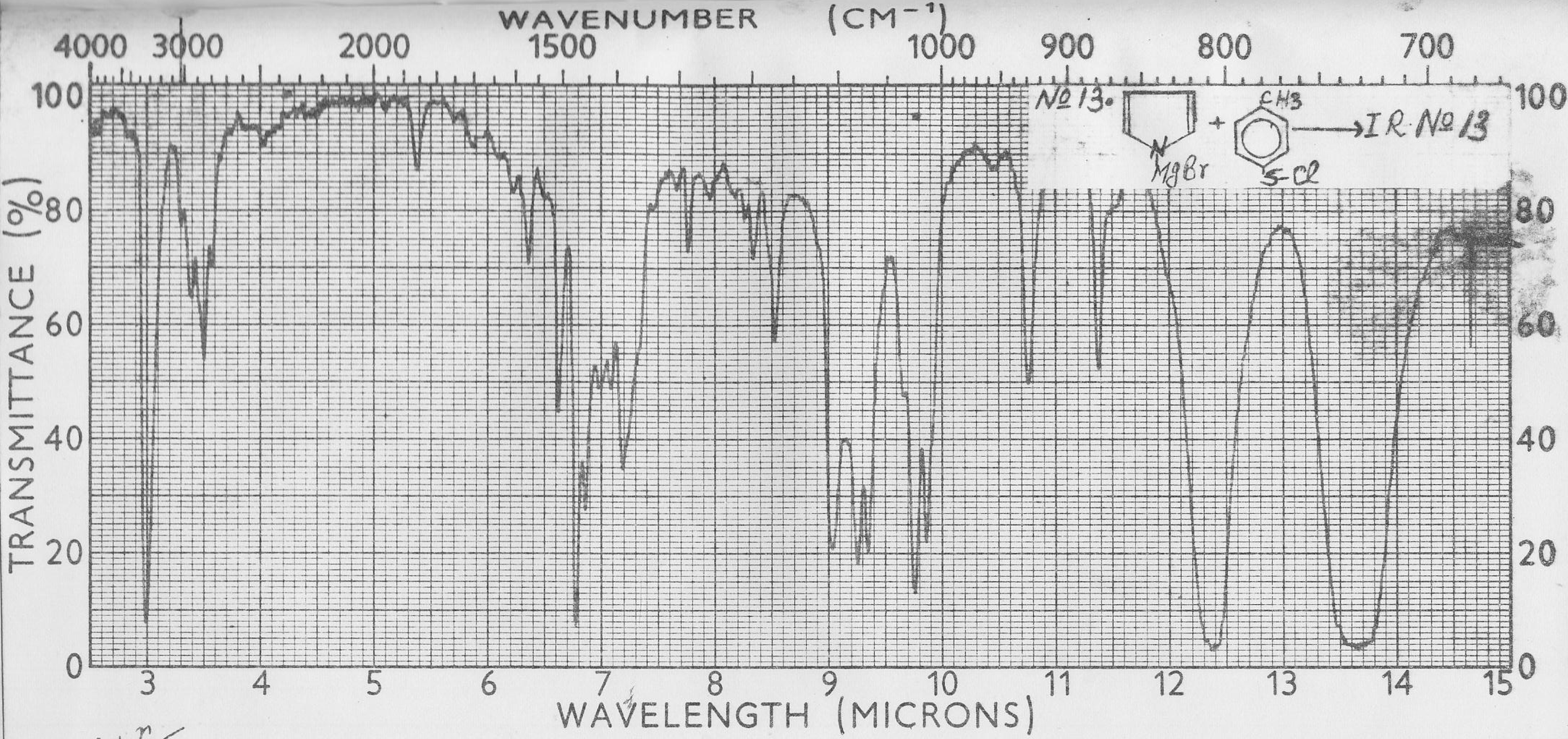
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