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To the Committee on Graduate Study:

I submit herewith a thesis by Kenneth C. Hart, "Molecular Organic Compounds of Picryl Chloride." I recommend that this thesis be accepted for eighteen quarter hours credit in fulfillment of the requirements for the degree of Master of Science in Education.

C. A. Brautlecht

Major Professor

At the request of the Committee on Graduate Study, I have read this thesis and recommend its acceptance.

Judson A. Robertson

Accepted by the Committee

P. M. Hamer

Chairman

MOLECULAR ORGANIC COMPOUNDS

of

PICRYL CHLORIDE

A THESIS

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of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for
the Degree of
Master of Science in Education

Kenneth C. Hart

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PART I

INTRODUCTION

It has been known for a long period of time that two saturated organic compounds are capable of uniting to form a molecular or addition compound. This being true, the idea of the present valence theory must be modified. Of the newer theories advanced by numerous investigators none seems to entirely solve the problem. It remains for some one to present a theory which will explain the linkage of all addition compounds. With this as an ultimate aim, a series of investigations is being conducted in this laboratory, in an endeavor to give more accurate information concerning the formation of addition compounds. The first investigation of this nature, which was conducted by Alice Heap, was followed by that of Ferris U. Foster, J. C. Lowery, Wm. H. Lockwood, Alan Hisey, and Jesse H. Wood. When this series of researches on addition compounds is completed, it is hoped that more accurate information on the subject will be available and this would lead to a better understanding of the formation of these compounds.

Nitro compounds as well as amines, hydrocarbons, and phenols of the aromatic series are capable of forming molecular organic compounds. Most notable and numerous of these are the picrates, which are used widely as derivatives for the identification of organic compounds. Lowery conducted an investigation on molecular compounds of picric acid; Hisey, on 2,4-dinitrochlorobenzene; and Wood, on 2,4-dinitrobromobenzene.

In conducting an investigation of this kind, a thorough search of the literature must be made. This should be followed by the preparation, analyses, and determination of the physical properties of a number of the molecular compounds. This form of procedure should throw light on the valence relations and consequently aid in explaining the linkage of the compounds.

The physical data in the field of molecular compounds are inaccurate and incomplete. These compounds being unstable cause irregularities to occur in the literature as to the correct melting points of the ad-

dition compounds. For instance, in the case of the molecular compound of diphenylamine and picryl chloride one investigator gave the melting point as 65-66°, another as 63-64°, and still another as 62°. This case indicates that the melting points should be determined with a calibrated thermometer and stem corrections should be made. Therefore, it becomes necessary to carefully check the melting points of a number of the molecular compounds found in the literature.

It is also found that in many cases the molecular ratios are not given. To make the physical data pertaining to the compound as complete as possible it becomes necessary to analyze carefully the compounds prepared in order to determine the exact ratios in which the components combine to form the molecular compounds. One investigator announced that one molecule of carbazole forms a molecular compound with picryl chloride, the melting point being 60-65°. Another investigator reported that a molecular compound is formed with carbazole and picryl chloride; the melting point was given as 155°. Since the ratio was not stated in the latter case the information from the literature leaves much to be desired.

The purpose of this investigation on molecular compounds of picryl chloride may be stated as follows:

1. To collect from the literature all of the molecular compounds of picryl chloride which have been prepared and record the melting points and molecular ratios of these compounds.

2. To prepare some of the addition compounds of picryl chloride which have been found in the literature and attempt the preparation of other molecular compounds of picryl chloride with the more common organic compounds.

3. To determine the melting points of the addition compounds and check the irregularities that appear in the literature.

4. By careful analyses to determine the ratios in which the components combine to form the molecular compounds.

5. To determine if the molecular compound is the first step in the formation of a substitution compound.

6. To investigate the theories that have been advanced relative to the formation of molecular compounds, and to modify these theories so as to give a possible explanation of the linkage of molecular compounds of picryl chloride.

PART II

HISTORICAL

I. ADDITION COMPOUNDS OF PICRYL CHLORIDE

A large number of molecular compounds of picryl chloride were found in the literature. The first recorded ones were prepared by Liebermann and Palm[1], in 1875, using (1) naphthalene, (2) phenanthrene, (3) stilbene or symmetrical diphenyl ethylene and (4) fluorene. The above four components were heated in concentrated alcoholic solution with picryl chloride and the addition compounds crystallized out in large needles. These compounds consisted of one molecule of the second component and one molecule of picryl chloride. The molecular ratio was 1:1. Naphthalene picryl chloride, $C_{10}H_8.C_6H_2(NO_2)_3Cl$, formed long plate, canary yellow needles which melted at 95-96°C. Vilet[2], in 1924, prepared the same addition compound with naphthalene and picryl chloride but he gave its melting point as 94°. The phenanthrene picryl chloride,

1 Liebermann and Palm, Ber. 8, 378 (1875).
2 Vilet, Rec. trav. chim. 43, 606-35 (1924).

$C_{14}H_{10}.C_6H_2(NO_2)_3Cl$, crystallized in lemon yellow needles which melted at 88°. Stilbene picryl chloride, $C_{14}H_{10}.C_6H_2(NO_2)_3Cl$, formed dark yellow needles which melted at 70-71°. Fluorene picryl chloride, $C_{13}H_{10}.C_6H_2(NO_2)_3Cl$, consisted of orange needles which melted at 69-70°.

Mertens[3], in 1878, reported an addition compound of picryl chloride and benzene. It formed yellow needles which were very unstable. No melting point was given.

Hertz[4], in 1890, prepared the molecular compound of diphenylamine picryl chloride, $NH(C_6H_5)_2.2C_6H_2(NO_2)_3Cl$. He allowed one molecule of the amine to react with two molecules of the chloride in a 50% solution of alcohol. The addition compound was described as being deep-red needles and melting at 65-66°. Wedekind[5], in 1900, announced the formation of the same addition compound of diphenylamine and two molecules of picryl chloride. He stated that the molecular compound was probably the first stage of the reaction, the completion of which is hindered by "stereochemical" causes. The melting point was given as 63-64°. The compound was said to be slightly soluble in alcohol. Hantz[6], in 1910, reported the compound again. He gave the melting point as 62° and added

3 Mertens, Ber. 11, 884 (1887).
4 Hertz, Ber. 23, 2540 (1890).
5 Wedekind, Ber. 33, 426-436 (1900).
6 Hantz, Ber. 43, 1662 (1910).

that when it was treated with chloroform and petroleum ether it resolved into its constituents.

Wedekind[7], in 1900, not only formed an addition compound of picryl chloride and diphenylamine but he obtained as well an addition compound of carbazole and two molecules of picryl chloride, $C_{14}H_{12}N.2C_6H_2(NO_2)_3Cl$. The compound formed yellowish red needles which melted at 160-165°, and decomposed at 180°. The compound, as was stated in the case of diphenylamine picryl chloride, did not form a substitution product, probably due to "stereochemical" causes. One molecule of the carbazole and picryl chloride formed an addition compound according to the statement of Ciusa and Vecchiotti[8] by boiling the components in alcoholic solution. The addition compound, $C_{12}H_9N.C_6H_2(NO_2)_3Cl$, formed dark red needles which softened at 140° and melted at 155°.

According to Lemoult[9] picryl chloride combined with tertiary bases of the diphenylamine series to form colored addition compounds. He prepared the addition compound of picryl chloride and tetramethyldiaminodiphenylmethane which crystallized in dark black needles and

7 Wedekind, Ber. 33, 434 (1900).
8 Ciusa and Vecchiotti, Atti. R. Accad. Lincei. (V), 21, ii, 1661-166 (1912).
9 Lemoult, Compt. rend. 135, 346-348 (1902).

melted at 71°.

Wedekind[10], in 1902, isolated an addition compound of pyridine and picryl chloride, containing one molecule of each, from benzene solutions of the two components. Wedekind's compound had a melting point of 138° but the product hydrolyzed to form pyridine picrate and hydrochloric acid. The formation of the compound was a very slow process. Hodges[11], in 1926, made a comprehensive study of the reaction. He stated that picryl chloride reacts very slowly with anhydrous pyridine even at 70° but the speed increases with pyridine which has been specially dried. It was anticipated that alcohol would accelerate the reaction. The alcoholic solution deposited brown crystals which melted at 220°, and concentration of the remaining solution yielded pyridine picrate. This indicated that Wedekind's reaction was an intermediate one. In summarizing, Hodges stated that the reaction between picryl chloride and pyridine in alcoholic solution is bimolecular and results in the slow formation of an ionized addition compound, picryl pyridinium chloride. The quantity of this compound

10 Wedekind, Ann. 313, 257 (1902).
11 Hodges, J. Chem. Soc. 2417 (1926).

produced depends on the concentration of the reactants and on the temperature.

Sudborough and Picton[12], in 1906, reported that trinitrobenzene and various trinitro derivatives formed addition compounds with α- and β-naphthylamines and other arylamines, including primary, secondary and tertiary bases. Certain of these addition compounds can be alkylated, acetylated and benzoylated, and all can be resolved by mineral acids into their components. He prepared the addition compound of picryl chloride and α-naphthylamine. It crystallized from alcohol in long brown needles which melted at 110-111.5° and was extremely unstable, readily losing hydrogen chloride and forming picryl-α-naphthylamine. He was not able to prepare the addition compound of picryl chloride and β-naphthylamine; the product obtained in each experiment was picryl-β-naphthylamine. These investigators also reported that picryl chloride and ethyl-α-naphthylamine yielded an addition compound, $C_{10}H_7NH\ C_2H_5.C_6H_2(NO_2)_3Cl$, when the two components are separately dissolved in ether, the solutions mixed, and a small amount of alcohol added. The product crystallized in slender, silky, brown needles

12 Sudborough and Picton, J. Chem. Soc. 89, 583 (1906).

melting at 85°, and is readily soluble in cold ether or benzene but only sparingly so in cold alcohol. It is far more stable than the addition compound of α-naphthylamine and picryl chloride. Sudborough and Picton stated that picryl chloride and diethyl-β-naphthylamine formed an addition compound, $C_{10}H_7N(C_2H_5)_2.C_6H_2(NO_2)_3Cl$, which crystallized from warm alcohol in dark purple needles and melted at 77°. It dissolved readily in cold benzene yielding a reddish-purple solution but the color disappeared when the solution is diluted. Again, they mentioned that a similar addition compound, $C_{10}H_7N(CH_3)_2.C_6H_2(NO_2)_3Cl$, is obtained when dimethyl-α-naphthylamine is used as the second component. This molecular compound crystallized in slender, red needles and melted at 42°.

Bruni and Ferrari[13], in 1906, reported, as is shown below, a number of molecular compounds of picryl chloride with aromatic hydrocarbons.

(1) Diphenyl picryl chloride, molecular ratio 1:1.

(2) Diphenylmethane picryl chloride.

(3) Triphenylmethane picryl chloride, two compounds,

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13 Bruni and Ferrari, Chem. Ztg. 30, 568-69 (1906).

the ratios being 1:1 and 1:3.

(4) Diphenylethane picryl chloride, ratio 1:2.

(5) Stilbene picryl chloride[14], two compounds, the molecular ratios being 1:1 and 1:2.

(6) Diphenyl acetylene picryl chloride, two compounds, the molecular ratios being 1:1 and 1:2.

(7) Azobenzene picryl chloride, molecular ratio 1:2.

The melting point and color of the crystals were not given in any of these cases.

Ciusa and Agostinelli[15], in 1907, prepared a number of addition products of trinitrobenzene derivatives with certain aromatic nitrogen compounds. In this work they described several compounds formed from picryl chloride and the phenyl hydrazones of aromatic aldehydes. These compounds are sparingly soluble in ordinary solvents and exhibit gradations in color and solubility dependent on the different radicals present in the benzene nuclei of the original aldehydes. The radicals also influence the stability of the addition products. The phenylhydrazones

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14 The addition compounds of stilbene were first reported by Liebermann and Palm, a discussion of which has been previously given.

15 Ciusa and Agostinelli, Atti. R. Accad. Lincei. (V), 16, i, 409-412 (1907).

exhibit behavior analogous to that of the secondary amines. The addition compounds of picryl chloride and the phenylhydrazones are briefly summarized: (1) Benzaldehydephenylhydrazone gave the compound, $C_{13}H_{12}N_2 \cdot 2C_6H_2(NO_2)_3Cl$, which crystallized from alcohol in dark maroon, shining needles having a melting point of 90-91°. (2) Piperonaldehydephenylhydrazone gave the compound, $C_{13}H_{12}N_2 \cdot 2C_6H_2(NO_2)_3Cl$, which crystallized from alcohol in almost black, shining needles. The melting point was 123°. The compound is very slightly soluble in cold water. (3) Anisaldehydephenylhydrazone gave the compound, $C_{14}H_{14}ON_2 \cdot 2C_6H_2(NO_2)_3Cl$, which crystallized in shining, black, flattened needles having a melting point of 92°. (4) m-Nitrobenzaldehydephenylhydrazone yielded the compound, $C_{13}H_{11}O_2N_3 \cdot 2C_6H_2(NO_2)_3Cl$, which formed shining, brick-red needles with a melting point of 105°. (5) Cinnamaldehydephenylhydrazone yielded the compound, $C_{12}H_{14}N_2 \cdot 2C_6H_2(NO_2)_3Cl$, which separated into minute, brick-red needles. The melting point first given as 112-113° was later corrected to 122-123°. It is sparingly soluble in alcohol. (6) α-Methylindole gave the compound $C_9H_9N_2 \cdot 2C_6H_2(NO_2)_3Cl$, which crystallized from alcohol in long, dark-red needles having a melting point of 115-116°. (7) β-Methylindole gave the compound, $C_9H_9N \cdot 2C_6H_2(NO_2)_3Cl$, which formed long, dark-red needles.

The melting point was originally given as 112-113° but later it was changed to 120°. Later, in 1912, Ciusa and Vechiotti[16] stated that picryl chloride derivatives of the α and β-methylindoles had only one molecule of the chloride instead of two.

Ciusa and Padoa[17], in 1909, reported that m-nitrobenzaldehydephenylmethylhydrazone, which occurs in two modifications, formed with picryl chloride an addition compound which undergoes a considerable amount of dissociation even in concentrated alcoholic solution, giving the red hydrazone. The melting point was not given.

Busch and Kogel[18], in 1910, described an addition compound of methyl-α-naphthylamine and picryl chloride. They stated that when the two components are boiled in alcoholic solution for a short time, methyl-α-naphthylamine picryl chloride is formed, $C_{10}H_7NHCN_3.C_6H_2(NO_2)_3Cl$. The compound had long, dark-red, silky-lustrous, interlaced needles which melted at 94°.

Boeris[19], in 1911, in the crystallography of some

16 Ciusa and Vecchiotti, Atti. R. Accad. Lincei. (V), 21, ii, 161-166 (1912).
17 Ciusa and Padoa, Atti. R. Accad. Lincei. (V), 18, ii, 621-626 (1909).
18 Busch and Kogel, Ber. 43, 1549-64 (1910).
19 Boeris, Zeitsch, Kryst. Min. 49, 72-73 (1911).

organic addition compounds stated that isoapiole and picryl chloride formed the molecular compound, $C_{12}H_{14}O_4 \cdot C_6H_2(NO_2)_3Cl$, from alcohol or ether solution. This addition compound formed dark, garnet-red, triclinic crystals, melting at 55-56°.

Ciusa and Vecchiotti[20], in 1911, prepared a number of addition compounds of picryl chloride. (1) Benzaldehyde-p-nitrophenylhydrazone formed a compound $C_6H_5CH{:}N.NH\ C_6H_4NO_2 . 2\ C_6H_2(NO_2)_3Cl$, which crystallized in red carmine needles. The melting point was given as 132°. (2) The compound benzaldehydephenylmethylhydrazone formed $C_6H_5CH{:}NCH_3C_6H_5 . 2C_6H_2(NO_2)_3Cl$, which crystallized in dark red needles; the melting point was 65°. (3) The compound m-nitrobenzaldehydephenylhydrazone formed $NO_2C_6H_4CH{:}N.NH\ C_6H_5 . C_6H_2(NO_2)_3Cl$, which had dark-red needles and melted at 98°. (4) The compound piperonaldehydephenylmethylhydrazone formed a complex addition product, $CH_2{:}O{:}C_6H_3CH.N{:}CH_3C_6H_5 . C_6H_2(NO_2)_3Cl$, which crystallized in black needles with a violet luster, and had a melting point of 115°. They also stated that an addition compound of a very unstable nature was obtained with m-nitrobenzaldehydemethylhydrazone. The melting point was not given.

Ciusa and Vecchiotti, Atti. R. Accad. Lincei (V), 20, ii, 377-383 (1911).

Other addition compounds were obtained by Ciusa and Vecchiotti[21] in 1911. They stated that 2,3-dimethylindole formed with picryl chloride an addition compound, $C_{10}H_{11}N.C_6H_2(NO_2)_3Cl$, which had dark red needles and melted at 140°. Tetrahydrocarbazole and picryl chloride formed chocolate brown needles which melted at 121°. The addition compound with carbazole has already been mentioned. The last addition compound reported of this investigation was phenyl indole and picryl chloride, $C_{14}H_{11}N.C_6H_2(NO_2)_3Cl$. The compound consisted of carmine red needles and melted at 119°. They formed the above compounds by the interaction of the components either alone or in boiling alcoholic solution.

Von Walther and Roch[22], in 1923, formed a very complex addition compound of picryl chloride and 4-phenyl-2-p-tolylaminothiazole. The compound, $C_{16}H_{14}N_2S.C_6H_2(NO_2)_3Cl$, consisted of red crystals and melted at 90°. It decomposed by alkalies into its components.

Lesser[23], in 1914, in his work on methylnaphthalene

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21 Ciusa and Vecchiotti, loc cit.
22 Von Walther and Roch, J. prakt. chem. 87, 27-66 (1913).
23 Lesser, Ann. 402, 1-51 (1914).

found that picryl chloride and a derivative of α-methylnaphthalene, 4-chloro-1-amino-2-methylnapthalene, formed an addition compound which consisted of brown-red needles and melted at 119°. An addition compound was also formed with 1-amino-2-methylnaphthalene and picryl chloride. The compound consisted of dark, brownish red needles which melted at 129-130°. Another addition product of dimethyl aniline and picryl chloride was given. This compound, $C_8H_{11}N.C_6H_2(NO_2)_3Cl$, consisted of red needles and melted at 68°. The compound was very unstable and upon standing in moist air it gave the yellow substitution product which melted at 212°.

Efremov[24], in 1918, constructed binary fusion diagrams for mixtures of picryl chloride and various hydrocarbons and picric acid. Equimolecular compounds formed in each case with the former, while with the latter a solid solution was observed. The following compounds were obtained: (1) anthracene picryl chloride, brown red needles, melting at 141.6°; (2) acenaphthene picryl chloride of orange crystals melting at 113.2°; (3) acenaphthylene picryl chloride, orange colored crys-

24 Efremov, J. Russ. Phys. Chem. Soc. 50, 421-440 (1918).

tals, melting at 109.4°; (4) retene picryl chloride, yellow brown crystals, melting at 53.5°. He also prepared naphthalene picryl chloride, phenanthrene picryl chloride, and fluorene picryl chloride giving their melting points as 91.2°, 82.4°, and 64.6° respectively. These last three compounds were isolated by Liebermann and Palm in 1875[25].

Efremov and Tikhomirova[26], in 1928, possibly formed a molecular compound of picryl chloride and tetryl, a hydrocarbon. The melting point was given as 81.2°. They also prepared a possible molecular compound of picryl chloride and trinitro-m-xylene. The melting point was not given.

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25 Liebermann and Palm, loc. cit.
26 Efremov and Tikhomirova, Ann. Inst. Anal. Phys. Chem. 4, 92-117 (1928).

II. SUBSTITUTION COMPOUNDS OF PICRYL CHLORIDE.

In examining the literature a very large number of substitution compounds of picryl chloride were found recorded. It is the opinion of many investigators, notably Kekule[27], that addition compounds constitute the first step in the formation of substitution compounds. If this be true, it is of interest to make a thorough investigation of the substitution compounds of picryl chloride in order to arrive at something definite in regard to the relation of addition compounds and substitution compounds.

Austen[28], in 1874, prepared the first recorded substitution compounds of picryl chloride. He stated that when picryl chloride and m-nitraniline are dissolved in boiling alcohol, a substitution reaction takes place forming picryl-m-nitraniline. This compound crystallized from glacial acetic acid in small yellow-orange transparent crystals which melted at 205°.

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27 Kekule, Organische Chemie, Fred. Enke. (1867).
28 Austen, Ber. 7, 1248 (1874).

By an analogous method picryl-p-nitraniline was formed and melted at 216°. This compound closely resembled the previously described isomer but is slightly more soluble in most solvents. Later, in 1900, Wedekind[29] prepared the same substitution compounds. He gave the melting point of picryl-m-nitraniline as 202-203°, and that of picryl-p-nitraniline as 214-215°.

Romburg[30], in 1883, described a number of substitution compounds of picryl chloride. He added methylamine to an alcoholic solution of picryl chloride and a substitution reaction took place forming methylpicramide which melted at 110-111°. Likewise, dimethylpicramide melting at 138°, ethylpicramide melting at 84°, and diethylpicramide, having orange colored crystals melting at 163-164°, were prepared.

Again, in 1885, Romburg[31] announced other complex substitution compounds of picryl chloride. He prepared trinitrophenylpropylamine by the interaction of picryl chloride and propyl amine in alcohol. It formed red needles and melted at 59°. Trinitrophenylisobutylamine having red needles and melting at 95°, and trinitro-

29 Wedekind, Ber 33, 426-436 (1900).
30 Romburg, Rec. trav. chim. 2, 105 (1883).
31 Romburg, Rec. trav. chim. 4, 191 (1885).

phenylallylamine melting at 80° were prepared by an analogous method.

Michael and Browne[32], in 1887, prepared dipicryl hydroxylamine by treating an alcoholic solution of picryl chloride with an aqueous solution of hydroxylamine. The compound, $(C_6H_6O_6N_3Cl)_2N.OH$, formed yellow needles soluble in alcohol. The melting point was not given.

Willgerodt and Ferko[33], in 1888, described the preparation of picrylphenylhydrazine. They stated that it is best prepared by carefully mixing one molecule of picryl chloride and two molecules of phenylhydrazine in cold alcoholic solution. The compound formed red scales which melted at 172°. The investigators failed in their attempt to prepare unsymmetrical picryl hydrazine by heating picryl chloride and phenylhydrazine in alcoholic solution. E. Fisher[34], in 1889, prepared the above substitution compound which melted at 172°.

Willgerodt[35], in 1890, stated that symmetrical

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32 Michael and Browne, J. prakt. Chem. 35, II, 358-59 (1887).
33 Willgerodt and Ferko, J. prakt. Chem. 37, II, 345-358 (1888).
34 E. Fisher, Ann. 253, 1-5 (1889).
35 Willgerodt, J. prakt. Chem. 40, II, 264-270 (1890).

picryl hydrazines are obtained by the interaction of molecular proportions of picryl chloride and the hydrochloride of the aromatic hydrazine in alcohol at ordinary temperatures. The following substitution compounds were obtained: (1) symmetrical picrylhydrazine, (2) picryl-o-tolylhydrazine, (3) picryl-p-tolylhydrazine, and (4) picryl-α-naphthylhydrazine. Willgerodt[36], in 1891, prepared the picryl-α-naphthylhydrazine with the assistance of Schultz. They stated that it existed in two forms and decomposed at 176°.

Turpin[37], in 1891, prepared picryl-aniline from picryl chloride and aniline in alcohol. The compound melted at 177.5°. o-Picramidophenol was prepared by the interaction of orthoamidophenol and picryl chloride in boiling benzene. It consisted of crimson needles which melted at 175°.

Later, in 1891, Willgerodt and Bohm[38] announced the preparation of picryl-p-chlorophenylhydrazine in two modifications. The first was formed by warming together molecular proportions of 4-chlorophenylhydrazine and picryl chloride in alcoholic solution.

36 Willgerodt and Schultz, J. prakt. Chem. 43, II, 177-189 (1891)
37 Turpin, J. Chem. Soc. 59, 714 (1891).
38 Willgerodt and Bohm, J. prakt. Chem. 43, II, 482-496 (1891)

It crystallized from organic solvents in well-formed prisms and decomposed at 174-175°. The other was obtained by dissolving the chlorophenylhydrazine and picryl chloride in cold chloroform, and shaking the mixed solutions in the cold. The compound crystallized out as an amorphous mass. In recrystallization from cold chloroform, slender, yellow needles which decomposed at 170-171° were formed.

Again, in 1891, Willgerodt and Schultz[39] prepared (1) picryl-α-naphthylhydrazine and (2) picryl-β-naphthylhydrazine by the action of alcoholic solutions of picryl chloride on the naphthylhydrazines. The former had been previously prepared by Willgerodt[40]. Both of these compounds decomposed before melting, the latter at 175°.

Willgerodt and Ellon[41], in 1891, prepared (1) picryl-p-bromophenylhydrazine and (2) picryl-o-chlorophenylhydrazine. The former compound was formed from a hot, alcoholic solution of two molecules of the hydrazine and one molecule of picryl chloride. It crystallized in red prisms and melted at 160°.

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39 Willgerodt and Schultz, loc. cit.
40 Willgerodt, loc. cit.
41 Willgerodt and Ellon, J. prakt. Chem. 44 II, 67-77 (1892).

Willgerodt and Muhe[42], in 1892, prepared picryl-m-chlorophenylhydrazine. The compound crystallized in small, red prisms and decomposed at 177-178°. It dissolved in glacial acetic acid, benzene, hot ether, chloroform, but only sparingly in alcohol.

Curtius and Decdichen[43], in 1895, reported that picryl chloride reacted violently with hydrazine hydrate to form picryl hydrazine. It consisted of reddish-brown crystals which melted at 186°.

Purgotti[44], in 1896, prepared picrylmethylsalicylate by boiling picryl chloride and methyl sodiosalicylate in toluene solution. The compound formed yellow crystals which melted at about 139°.

Willgerodt and Klein[45], in 1899, prepared picryl-m-xylylhydrazine by the action of picryl chloride on m-xylylhydrazine. The compound crystallized from alcohol in slender, yellow needles, and dissolved in most organic solvents.

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42 Willgerodt and Muhe, J. prakt, Chem. 44, II, 451-466 (1892).
43 Curtius and Decdichen, J. prakt. Chem. 50, II, 241-247 (1894).
44 Purgotti, Gazzetta 26, II, 554-559 (1896).
45 Willgerodt and Klein, J. prakt, Chem. 60, II, 97-112 (1899).

Wedekind[46], in 1900, obtained a large number of substitution compounds of picryl chloride. In his work on the "stereochemical" observation of the reaction between picryl chloride and aromatic amines, he stated that of the various monosubstituted primary amines, the para compounds form the picryl derivatives most readily followed by the meta and then the ortho compounds, although there is not much difference between them. The nitro group forms an exception sincem for example, m-nitroaniline formed a picryl derivative with greatest ease and the o-nitroaniline only with great difficulty. The "stereochemical" influence of the ortho position was shown by picrylaminoacetophenone, of which the para compound easily formed a phenylhydrazone, while the ortho compound did not react with phenyl hydrazine. Compounds of the phenylene-diamine type formed only mono picryl derivatives, while those of the benzidine series formed dipicryl derivatives which, curiously, are soluble in alkalies and precipitated by acids. The following picryl derivatives were prepared by treating two molecules of the amine with one molecule of picryl chloride:

(1) o-Picrylaminobenzoic acid, M. P. 271-272°.

(2) m-Picrylaminobenzoic acid, M. P. 233-234°.

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46 Wedekind, Ber. 33, 426-436 (1900).

(3) p-Picrylaminobenzoic acid, M. P. 292-293°.

(4) o-Picrylnitraniline, M. P. 220°.

(5) o-Picrylchloroaniline, M. P. 158-159°.

(6) m-Picrylchloroaniline, M. P. 169-170°.

(7) p-Picrylaminoacetophenone, M. P. 162-163°.

(8) o-Picrylaminoacetophenone, M. P. 232°.

(9) o-Picrylaminobenzaldehyde, M. P. 203-205°.

(10) m-Picrylaminophenol, M. P. 203-204°.

(11) p-Picrylaminoacetanilide, M. P. 240-242°.

(12) Picrylethylaniline, M. P. 105-107°.

(13) Picrylpiperidine, M. P. 104-106°.

(14) p-Picrylaminophenol, M. P. 172-173°.

Bamburger and Muller[47], in 1900, reported the preparation of picryl-β-naphthylamine. The compound was prepared from picryl chloride and β-naphthylamine in alcoholic solution. It crystallized from acetic acid in glistening, coral-red prisms which melted at 233-233.5°. Sudborough and Picton[48], in 1906, prepared the same compound by an analogous method. They gave its melting point as 231.5°.

Willgerodt and Herzog[49], in 1905, obtained s-picryl-

47 Bamburger and Muller, Ber. 33, 110-113 (1900).
48 Sudborough and Picton, J. Chem. Soc. 89, 594 (1906).
49 Willgerodt and Herzog, J. prakt, Chem. 71, II, 385-398 (1905).

γ-cumylhydrazine, by the action of picryl chloride and 2, 4, 5-trimethylphenylhydrazine-γ-cumylhydrazine in alcoholic solution. It was easily soluble in chloroform, benzene, and carbon disulphide.

Willgerodt and Lindenburg[50], in 1905, announced the formation of a very complex substitution compound of picryl chloride by its action on p-xylylhydrazine in alcoholic solution. Symmetrical-picryl-p-xylylhydrazine was prepared which crystallized in small, red, slender needles, melting with decomposition at 169°.

Ciusa and Agostinelli[51], in 1906, reported that the phenylhydrazones of acetone, propylaldehyde, and camphor and probably those of the aliphatic aldehydes and ketones, readily yield crystalline picrates, the formation of which may be used for characterizing small quantities of aldehydes and ketones of the aliphatic series. The following compounds were formed with picryl chloride:

(1) Acetonephenylhydrazonepicrate, yellow needles, melting at 81-82°.

(2) Camphor phenylhydrazonepicrate, golden-yellow needles, melting at 137° to form a black liquid.

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50 Willgerodt and Lindenburg, J. prakt. Chem. 71, II, 398-409 (1905).

51 Ciusa and Agostinelli, Atti. R. Accad. Lincei (V), 15, ii, 238-242 (1906).

(3) Propaldehydephenylhydrazonepicrate, canary-yellow needles, melting at 156-157°.

(4) Trinitrohydrazobenzene, melting at 186-187°.

(5) Benzaldehydetrinitrophenylhydrazone, melting at 273-274°.

(6) Piperonaldehydetrinitrophenylhydrazone, dark-red crystals, melting at 169°.

Sudborough and Picton[52], in 1906, prepared picryl-α-naphthylamine by the interaction of picryl chloride and naphthylamine in alcoholic solution. The compound melted at 197-198°. Picrylmethyl-α-naphthylamine was obtained when picryl chloride and methyl-α-naphthylamine were boiled in alcohol for one hour. This compound crystallized from glacial acetic acid in glistening, black plates which melted at 245°.

Leeman and Grandmaugin[53], in 1908, announced the formation of picryl-m-toluidine by the interaction of m-toluidine and picryl chloride in alcoholic solution. The compound crystallized from alcohol in golden needles which melted at 126°. Busch[54], in 1909, formed the same compound. He stated that there are two modifications, a

52 Sudborough and Picton, J. Chem. Soc. 89, 594 (1906).
53 Leeman and Grandmaugin, Ber. 41, 1305 (1908).
54 Busch, J. Chem. Soc. 96, 564 (1909).

mixture of yellow prisms which melted at 130° and orange red needles which melted at 163°. Another substitution product was obtained with picryl chloride and 2,4-dinitrophenylhydrazine. Likewise, picryl-o-phenylenediamine was prepared which melted at 177-178°.

Busch and Pungs[55], in 1909, stated that when alcoholic solutions of picryl chloride and the following amines are mixed, the picrylamine is deposited frequently in two differently colored forms. (1) p-Toluidine gave a mixture of labile, yellow prisms which melted at 163°, and blood-red needles which melted at 165°. The former was obtained alone by treating the alkaline alcoholic solution of the mixture with hydrochloric acid, while the red form separated when the mixture was crystallized from alcohol and benzene. (2) p-Xylidine gave only blood-red needles which melted at 165°, but the laible form was obtained by acidifying the cold, alcoholic solution. (3) 1,3,4-Xylidine and picryl chloride gave orange-red monoclinic needles which melted at 158°. (4) 1,3,2-Xylidine yielded only citron-yellow leaflets which melted at 212°. (5) γ-Cumidine gave a product which separated from acetone in blood-red, dichroic needles and melted at 160°. It gave from alcohol, containing hydro-

55 Busch and Pungs, J. prakt. Chem 79, II 546-554 (1909).

chloric acid, needles which melted at 160° but which possessed a lighter color. (6) o- and p-Anisidines formed only orange-red, rhombic needles which melted at 142° and 138° respectively. (7) o- and p-Phenetidines gave, with picryl chloride, scarlet needles melting at 136° and 137°; the red needles melted at 123° and 124° respectively. (8) Methyl aniline gave a substitution product with picryl chloride which melted at 108-110°.

Pallak[56], in 1918, announced the formation of 4-picrylthiol-1-ethylbenzene from picryl chloride and 1-ethylbenzene-4-thiolaceticacid. The compound formed deep-yellow silky needles which melted at 113.5-116°.

Kehrmann, Ramm and Schmajewski[57], in 1921, prepared a number of substitution products of picryl chloride.

(1) 2,4,6-Trinitrophenyl-o-toluidine, orange-colored prisms, melting at 164°.

(2) Trinitrophenyl-o-aminodiphenylmethane, orange-colored crystals, melting at 140°.

(3) 2,4,6-Trinitrophenyl-o-cumidin, orange-colored crystals; no melting point given.

(4) 2, 4,6-Trinitro-o-aminotriphenylmethane, orange-colored crystals, melting at 180°.

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56 Pallak, Monatsh. 39, 179-200 (1918).
57 Kehrmann, Ramm and Schmajewski, Mitt. Helv. Chim. Acta. 2, 379 (1921).

Auwers and Allardt[58], in 1924, reported the formation of picryl indazole by mixing picryl chloride and indazole in alcoholic solution. The compound gave golden, rhombic plates which melted at 208-210°.

Giua[59], in 1925, announced that when picryl chloride and an excess of aqueous cyanamide are heated on a water bath, cooled and acidified with dilute hydrochlorid acid, picrylcyanamide and dipicryldicyandiamide are formed. The former compound is very unstable while the latter melts and decomposes at 254-255°. If the dipicrylguanidine is boiled in alcohol with concentrated hydrochloric acid, phenyl urea, which is yellow and melts with decomposition at 201-203°, is formed.

Giua and Petronia[60], in 1925, reported the formation of two substitution compounds of picryl chloride. (1) Picrylsemicarbazide is formed when picryl chloride and semicarbazide are heated together in alcohol. The compound crystallized in yellow crystals which melted and decomposed at 218-219°. (2) Picrylsemioxamazide was prepared in the same manner. It formed yellow crystals which melted and decomposed at 249-250°.

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58 Auwers and Allardt, Ann. 438, 1-33 (1924).
59 Giua, Gazz. Chim. Ital. 55, 662-665 (1925).
60 Giua and Petronia, J. prakt. Chem. 110, II 289-308 (1925).

Chronological arrangement of the addition compounds of picryl chloride that were found in the literature, including the molecular ratio, the melting point, and the color of the crystals.

Second Component	Molecular Ratio	Melting Point	Color and Crystalline Form
1. Naphthalene	1:1	90-96°	Canary-yellow needles
2. Phenanthrene	1:1	88°	Lemon-yellow needles
3. Stilbene	1:1	70-71°	Dark-yellow needles
4. Fluorene	1:1	69-70°	Orange-colored needles
5. Benzene	1:1	____	Yellow-needles
6. Diphenylamine	2:1	62-66°	Deep-red needles
7. Carbazole	2:1	160-165°	Yellowish-red needles
8. Carbazole	1:1	155°	Dark-red needles
9. 4,4-Tetramethyldiamino-diphenylmethane	___	71°	Dark-black needles

____ Indicates not given in the literature.

Second Component	Molecular Ratio	Melting Point	Color and Crystalline Form
10. Pyridine	1:1	138°	Brown crystals
11. α-Naphthylamine	___	110-111.5°	Brown needles
12. Ethyl-α-naphthylamine	1:1	85°	Silky, brown needles
13. Diethyl-β-naphthylamine	1:1	77°	Dark, purple-colored needles
14. Dimethyl-α-naphthylamine	1:1	42°	Slender, red needles
15. Diphenyl	1:1	___	_____
16. Diphenylmethane	1:1	___	_____
17. Triphenylmethane	1:1	___	_____
18. Triphenylmethane	3:1	___	_____
19. Diphenylethane	2:1	___	_____
20. Stilbene	2:1	___	_____
21. Diphenylacetylene	1:1	___	_____
22. Diphenylacetylene	2:1	___	_____
23. Azobenzol	2:1	___	_____

	Second Compound	Molecular Ratio	Melting Point	Color and Crystalline Form
24.	Benzaldehydephenyl-hydrazone	2:1	90-91°	Dark maroon shining needles
25.	Piperonaldehydephenyl-hydrazone	2:1	123°	Almost black needles
26.	Anisaldehydediphenyl-hydrazone	2:1	92°	Shining black needles
27.	m-Nitrobenzaldehyde-phenylhydrazone	2:1	105°	Brick-red needles
28.	Cinnamaldehydephenyl-hydrazone	2:1	122-123°	Brick-red needles
29.	α-Methylindole	1:1	115-116°	Long, dark-red needles
30.	β-Methylindole	1:1	120°	Long, dark-red needles
31.	m-Nitrobenzaldehyde-phenylmethylhydrazone	——	——	——————
32.	Methyl-α-naphthylamine	1:1	94°	Dark-red silky needles
33.	Isoapiole	1:1	55-56°	Dark, garnet-red needles
34.	Benzaldehyde-p-nitro-phenylhydrazone	2:1	132°	Red-carmine needles

	Second Component	Molecular Ratio	Melting Point	Color and Crystalline Form
35.	Benzaldehydephenyl-methylhydrazone	1:1	65°	Dark-red needles
36.	m-Nitrobenzaldehyde-phenylhydrazone	1:1	98°	Dark-red needles
37.	Piperonaldehydephenyl-methylhydrazone	1:1	115°	Black needles
38.	m-Nitrobenzaldehyde-methylhydrazone	---	---	---
39.	2,3-Dimethylindole	1:1	140°	Dark-red needles
40.	Tetrahydrocarbazole	---	121°	Chocolate-brown needles
41.	Phenylindole	1:1	119°	Carmine-red needles
42.	4-Phenyl-2-p-tolyl-aminothiazole	1:1	90°	Red crystals
43.	4-Chloro-1-amino-2-methylnaphthalene	1:1	119°	Brown-red crystals
44.	1-Amino-2-methyl-naphthalene	1:1	129-130°	Dark, brownish-red needles
45.	Dimethylaniline	1:1	68°	Red needles

Second Component	Molecular Ratio	Melting Point	Color and Crystalline Form
46. Anthracene	———	141.6°	Brown-red needles
47. Acenaphthene	———	113.2°	Orange-colored crystals
48. Acenaphthylene	———	109.4°	Orange-colored crystals
49. Retene	———	53.5°	Yellow-brown crystals
50. Tetryl	———	81.2°	———
51. Trinitro-m-xylene	———	———	———

Molecular compounds of picryl chloride found in the literature grouped under (1) hydrocarbons, (2) phenols, (3) amines, (4) nitro compounds, (5) hydrazones, and (6) nitrogen compounds.

I HYDROCARBONS

(Second Component)

1. Naphthalene
2. Phenanthrene
3. Stilbene (1:1)
4. Stilbene (2:1)
5. Fluorene
6. Benzene
7. Diphenyl
8. Diphenylmethane
9. Triphenylmethane (1:1)
10. Triphenylmethane (3:1)
11. Diphenylacetylene (1:1)
12. Diphenylacetylene (2:1)
13. Diphenylethane
14. Anthracene
15. Acenaphthene
16. Acenaphthylene

17. Retene

18. Tetryl

II NO ADDITION COMPOUNDS WITH PHENOL WERE FOUND IN THE LITERATURE.

III AMINES

1. Diphenylamine
2. Pyridine
3. 4,4-Tetramethyldiaminodiphenylmethane
4. α-Naphthylamine
5. Ethyl-α-naphthylamine
6. Diethyl-β-naphthylamine
7. Dimethyl-α-naphthylamine
8. Methyl-α-naphthylamine
9. 4-Phenyl-2-p-tolylaminothiazole
10. 4-Chloro-1-amino-2-methylnaphthalene
11. 1-Amino-2-methylnaphthalene
12. Dimethylaniline

IV NITRO COMPOUNDS

1. Trinitro-m-xylene

V HYDRAZONES

1. Benzaldehydephenylhydrazone
2. Piperonaldehydephenylhydrazone
3. Anisaldehydephenylhydrazone
4. Cinnamaldehydephenylhydrazone
5. m-Nitrobenzaldehydephenylmethylhydrazone
6. Benzaldehyde-p-nitrophenylhydrazone
7. Benzaldehydephenylmethylhydrazone
8. m-Nitrobenzaldehydephenylhydrazone
9. Piperonaldehydephenylmethylhydrazone
10. m-Nitrobenzaldehydemethylhydrazone
11. Isoapiole

VI. NITROGEN COMPOUNDS

1. α-Methylindole
2. β-Methylindole
3. Azobenzol
4. Carbazole (2:1)
5. Carbazole (1:1)
6. Tetrahydrocarbazole
7. 2,3-Dimethylindole
8. Phenylindole

Chronological arrangement of the substitution compounds of picryl chloride, together with their melting points, colors and crystalline forms. The substitution reaction took place between the organic compound and picryl chloride in alcoholic solution.

Substitution Compound	Melting Point	Color and Crystalline Form
1. Picryl-m-nitraniline	205°	Orange-yellow crystals
2. Picryl-p-nitraniline	216°	_____
3. Methyl picramide	110-111°	_____
4. Dimethylpicramide	138°	_____
5. Ethyl picramide	84°	_____
6. Diethylpicramide	163-164°	Orange-color crystals
7. Trinitrophenylpropylamine	59°	Red needles
8. Trinitrophenylisobutylamine	95°	Red needles

_____ Indicates not given in the literature.

Substitution Compound	Melting Point	Color and Crystalline Form
9. Trinitrophenylallylamine	80°	Crystals
10. Dipicrylhydroxylamine	___	Yellow needles
11. Picrylphenylhydrazine	172°	Pale-red scales
12. Symmetricalpicrylhydrazine	Decomp.	_____
13. Picryl-o-tolylhydrazine	Decomp.	_____
14. Picryl-p-tolylhydrazine	Decomp.	_____
15. Picryl-α-naphthylhydrazine	Decomp.	_____
16. Picrylaniline	177.5°	_____
17. Picryldiphenylaniline	62°	Soft, deep-red plates
18. o-Picramidophenol	175°	Crimson needles
19. Picryl-p-chlorophenyl-hydrazine (Two modifications)	Decomp. 174-175° Decomp. 170-171°	1. Well-formed prisms 2. Slender, yellow needles

Substitution Compound	Melting Point	Color and Crystalline Form
20. Picryl-β-naphthylhydrazine	Decomp. 175°	———
21. Picryl-p-bromophenyl-hydrazine	185-186°	Yellow-red, hexagonal crystals
22. Picryl-o-chlorophenyl-hydrazine	160°	Red prisms
23. Picryl-m-chlorophenyl-hydrazine	Decomp. 177-178°	Small, red prisms
24. Picrylhydrazine	186°	Deep, reddish-brown crystals
25. Picrylmethylsalicylate	139°	Yellow crystals
26. Picryl-m-xylylhydrazine	———	Yellow needles
27. o-Picrylaminobenzoicacid	271-272°	———
28. m-Picrylaminobenzoicacid	233-234°	———
29. p-Picrylaminobenzoicacid	292-293°	———
30. o-Picrylnitraniline	220°	———
31. o-Picrylchloroaniline	158-159°	———
32. m-Picrylchloroaniline	169-170	———

Substitution Compound	Melting Point	Color and Crystalline Form
33. p-Picrylaminoacetophenone	162-163°	———
34. o-Picrylaminoacetophenone	232°	———
35. o-Picrylaminobenzaldehyde	202-205°	———
36. m-Picrylaminophenol	203-204°	———
37. p-Picrylaminoacetanilide	240-242°	———
38. Picrylethylaniline	105-107°	———
39. Picryl piperidine	104-106°	Orange-red pyramid crystals
40. Picryl-p-aminophenol	172-173°	Crimson needles
41. Picryl-β-naphthylamine	231.5-233.5°	Coral-red prisms
42. S-Picryl-γ-cumylhydrazine	157.5°	———
43. S-Picryl-p-xylylhydrazine	Decomp. 169°	Small, red, slender needles
44. Acetonephenylhydrazone-picrate	81-82°	Unstable, yellow needles
45. Camphorphenylhydrazone-picrate	137°	Golden yellow

Substitution Compound	Melting Point	Color and Crystalline Form
46. Propaldehydephenylhydrazonepicrate	156-157°	Minute, canary-yellow needles
47. Trinitrohydrazobenzene	186-187°	———
48. Benzaldehydetrinitrophenylhydrazone	273-274°	———
49. Piperonaldehydetrinitrophenylhydrazone	169°	Dark-red crystals
50. Picryl-α-naphthylamine	197-198°	Crystalline plates
51. Picrylmethyl-α-naphthylamine	245°	Glistening, black plates
52. Picryl-m-toluidine (Two Modifications)	126° 163°	Golden needles Yellow prisms
53. Picryldinitrophenylhydrazine	———	———
54. Picryl-o-phenylenediamine	177-178°	———
55. Picryl-p-toluidine (Two modifications)	163° 165°	Yellow prisms Blood-red needles

Substitution Compounds	Melting Point	Color and Crystalline Form
56. Picryl-1-3-4-xylidine	158°	Orange-red, monoclinic needles
57. Picryl-p-xylidine	163°	Blood-red needles
58. Picryl-1-3-2-xylidine	212°	Citron-yellow leaflets
59. Picryl-γ-cumidine	160°	Blood-red needles
60. Picryl-o-anisidine	142°	Orange-red rhombic
61. Picryl-p-anisidine	138°	Orange-red, rhombic needles
62. Picryl-o-phenetidine (Two Modifications)	136° 123°	Scarlet needles Red needles
63. Picryl-p-phenetidine (Two Modifications)	137° 124°	Scarlet needles Red needles
64. Picrylmethylaniline	108-110°	Deep-red plates
65. 4-picrylthiol-1-ethyl-benzene	113.5-116°	Deep-yellow, silky needles
66. 2,4,6-Trinitrophenyl-o-toluidine	165°	Orange-colored prisms
67. Picryl-o-aminodiphenyl-methane	140°	Orange-colored prisms

Substitution Compound	Melting Point	Color and Crystalline Form
68. 2,4,6-Trinitrophenyl-o-cumidin	———	Orange-colored crystals
69. 2,4,6-Trinitro-o-amino-triphenylmethane	180°	Orange-colored crystals
70. Picrylcyanamide	unstable	———
71. Dipicryldicyandiamide	melts and decomp. 254-255°	———
72. Picrylsemicarbazide	melts and decomp. 218-219°	Yellow crystals
73. Picrylsemioxamazide	melts and decomp. 249-250°	Yellow crystals

PART III

EXPERIMENTAL

REAGENTS:-

An attempt was made to prepare addition compounds of picryl chloride with each of the following compounds:

1. Naphthalene
2. Fluorene
3. Diphenyl
4. Triphenylmethane
5. Anthracene
6. α-Naphthylamine
7. β-Naphthylamine
8. Benzidine
9. Aniline
10. Methylaniline
11. Dimethylaniline
12. o-Toluidine
13. p-Toluidine
14. o-Phenylenediamine
15. m-Phenylenediamine

16. p-Phenylenediamine
17. p-Aminophenol
18. Diethylamine
19. Triethylamine
20. Diphenylamine
21. Triphenylamine
22. Carbazole
23. Benzamide
24. Phthalimide
25. α-Naphthol
26. β-Naphthol
27. Hydroquinone
28. Pyrogallol
29. Resorcinol
30. Phenol
31. Catechol
32. o-Cresol
33. Phloroglucinol
34. Anisole
35. Pyridine
36. p-Bromoacetanilide
37. Guanidine nitrate
38. Urea

39. Thiourea

40. Benzene

41. Toluene

42. Phenanthrene

43. Diphenylmethane

44. m-Toluidine

45. p-Nitraniline

46. Xylidine

47. o-Xylene

48. m-Xylene

49. p-Xylene

Most of the materials were purchased from the Research Laboratory of the Eastman Kodak Company, practically all being of the highest purity. Aniline, methylaniline, and dimethylaniline were purified by distillation.

METHOD OF PREPARATION:-

The general method employed in preparing addition compounds was to weigh out the two components in molecular ratios, dissolve the mixture in boiling absolute alcohol, and allow the molecular compound to crystallize from the solution. The mother liquor was poured off long before crystallization was complete in order to prevent, as much as possible, the precipitation of impurities with the molecular compound. Then the crystals were placed on a filter paper so as to absorb the excess solvent. Recrystallization, in most cases, tended to cause decomposition of the compound, or a substitution compound was formed. For these reasons the compound had to be obtained as pure as possible with the first crystallization.

Alcohol could not be used as a solvent in all cases due to the insolubility of some of the components in it. Also, if there is a marked difference in the solubility of the two components in a solvent there is a tendency toward decomposition in that solvent. For this reason, carbon tetrachloride was used as a solvent in the preparation of the addition compounds of the α and β-naphthols. Benzene could not be used as solvent since an

addition compound was formed with it and picryl chloride.

When one of the components was a liquid, it was only necessary to dissolve the solid in the liquid component. The excess component evaporated and the molecular compound crystallized from the solution. It was then recrystallized from hot alcohol. A freezing mixture of ice and sodium chloride was used in some cases for low melting compounds in order to obtain the crystals. If the molecular compound was very unstable the components were mixed in the cold for boiling would tend to cause a substitution reaction to take place.

In some cases when the compound could not be obtained by the above methods, due to its low melting point, the formation of a molecular compound was indicated by a change in color of the solution or of the fused mixture. As an illustration, the fused mixture of picryl chloride and p-aminophenol had a very dark red color but it changed immediately to a bright golden color, due undoubtedly to the formation of a substitution compound. The color of the molecular compound is, in all cases observed, much deeper than that of either component.

DETERMINATION OF MELTING POINTS:-

The melting points of the compounds were determined by the capillary tube method described by Mulliken[61]. The neck of a 250cc. Pyrex distilling flask was cut off about three fourths of an inch from the bulb. A test tube, which fitted the flask, was cut off at the bottom to within an inch of the bottom of the flask, and the end was fused together to form a round bulb. The flask was filled about three-fourths full of sulfuric acid, and the test tu be, which was filled to about an inch above the level of the acid in the bulb, was inserted in the bulb. The thermometer was inserted in the test tube so that the bulb extended below the surface of the acid in the flask. A small capillary tube was filled with the compound by placing it in the crystals and then scratching it with a file. The vibration of the tube caused the compound to fall to the bottom. A cork was placed on the thermometer and the end of the capillary tube was inserted in the cork, causing it to cling to the bulb of the thermometer. A second thermometer was suspended so that its bulb

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61 Mulliken, "The Identification of Pure Organic Compounds, "Jonn Wiley and Sons, Inc., New York, Vol. I, p. 218 (1904)

reached the midway point of the stem emerging from the thermometer in the bath, in order to obtain the temperature of the emergent stem. It is desirable to have three melting point set-ups since the sulfuric acid cools very slowly.

The melting points were taken with thermometers calibrated by the Bureau of Standards. Thermometer number 43077, graduated in tenths of a degree, had a range from 0° to 100°; number 49971, graduated in two-tenths of a degree, had a range from -11° to 201°; and number 5860, graduated in two-tenths of a degree, had a range from 200° to 300°.

The formula for the stem correction for the thermometers, as given by the Bureau of Standards certificate accompaning each, is as follows:

Stem Correction = $.00016 \times n(T^{\circ} - t^{\circ})$

where n is the number of degrees emergent from the bath; T° is the temperature of the bath; and t° is the mean temperature of the emergent stem. Since the stem is at a lower temperature than the bath, the correction is to be added to the observed reading.

The absolute variation of the thermometer must be corrected according to the table prepared by the Bureau of Standards as given in the certificate accompaning each thermometer. The correction for any particular temperature must be obtained by interpolation, (see graphs on pages 56, 57, and 58). The correction is to be added or subtracted from the reading already corrected for stem exposure. The temperature corrected is the exact melting point of the compound.

The following tabulation gives a correction for the readings of the thermometers used:

Bureau of Standards No. 43077

Reading	Temperature	Cor. to Reading
0°	0.00°	.00°
20	19.98	-.02
40	39.89	-.11
60	59.95	-.05
80	79.98	-.02
100	100.16	+.16

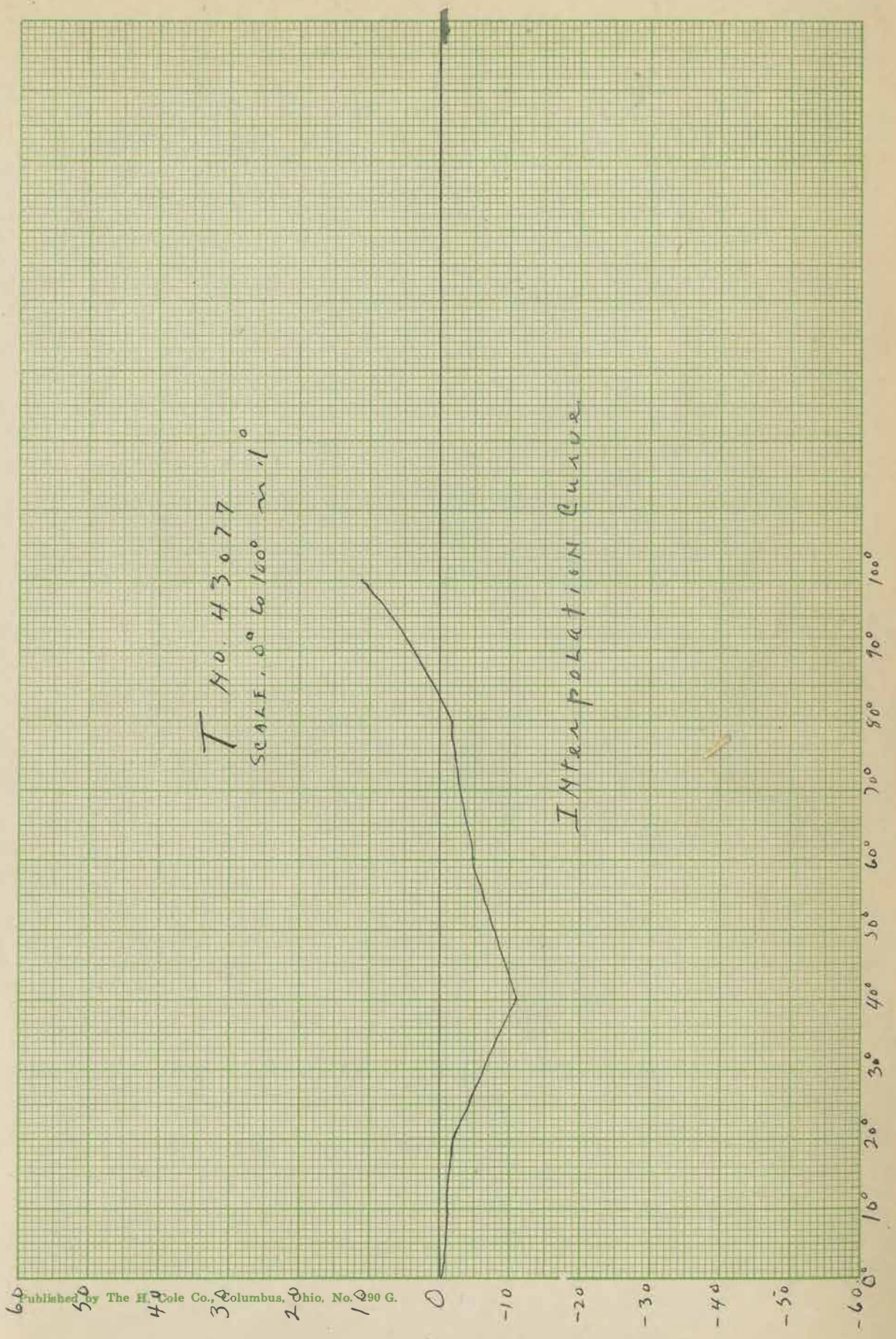
Bureau of Standards No. 49971

Reading	Temperature	Cor. to Reading
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20	19.98	-.02
40	39.96	-.04
60	59.96	-.04
80	79.98	-.02
100	99.92	-.08
120	119.92	-.08
140	139.90	-.10
160	159.70	-.30
180	179.52	-.48
200	199.42	-.58

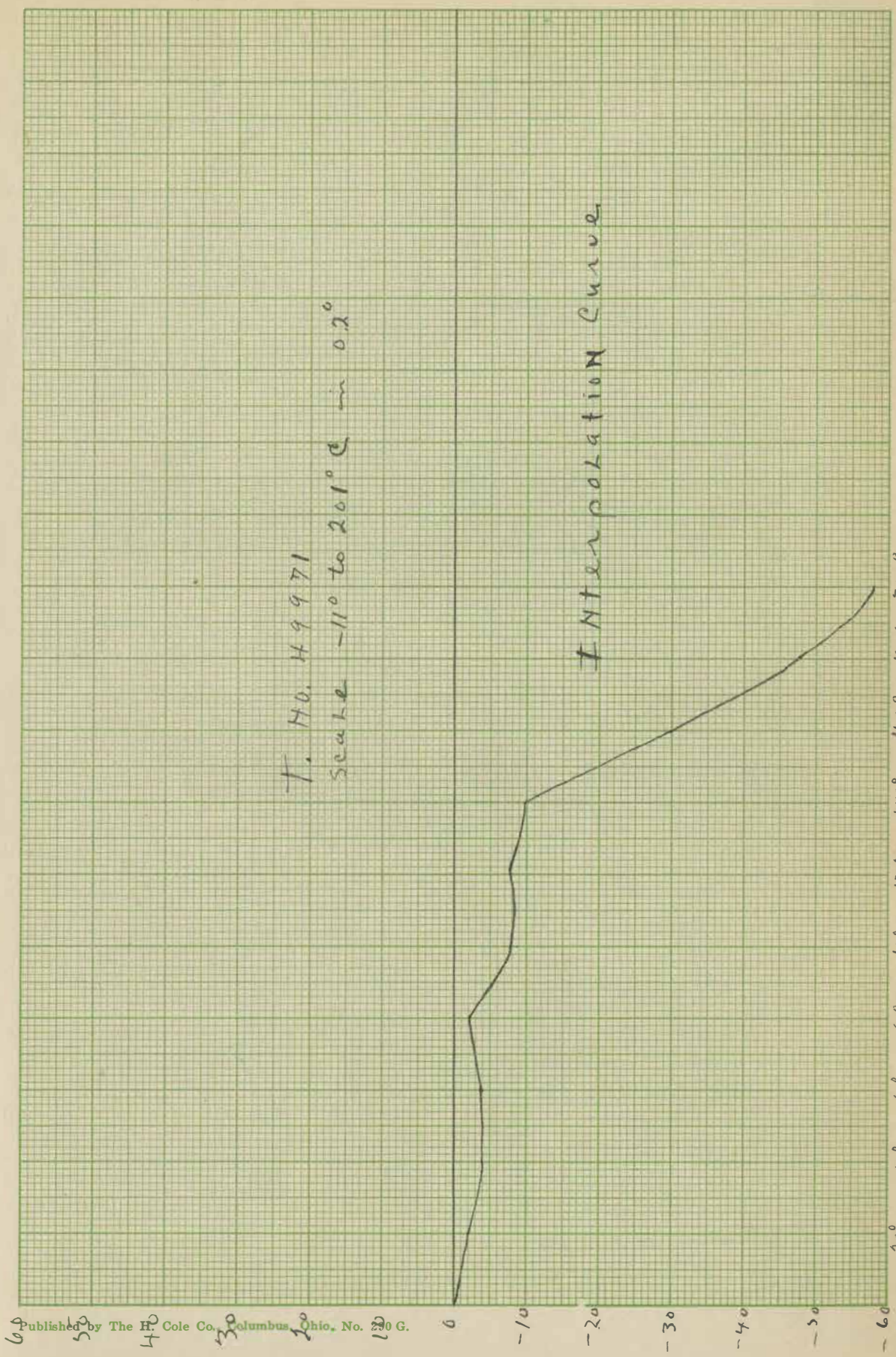
Bureau of Standards No. 5860

Reading	Temperature	Cor. to Reading
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100	100	.0
210	210	.0
220	220	.0
240	240.1	+ .1
260	260.2	+ .2
280	280.3	+ .3
300	299.9	- .1

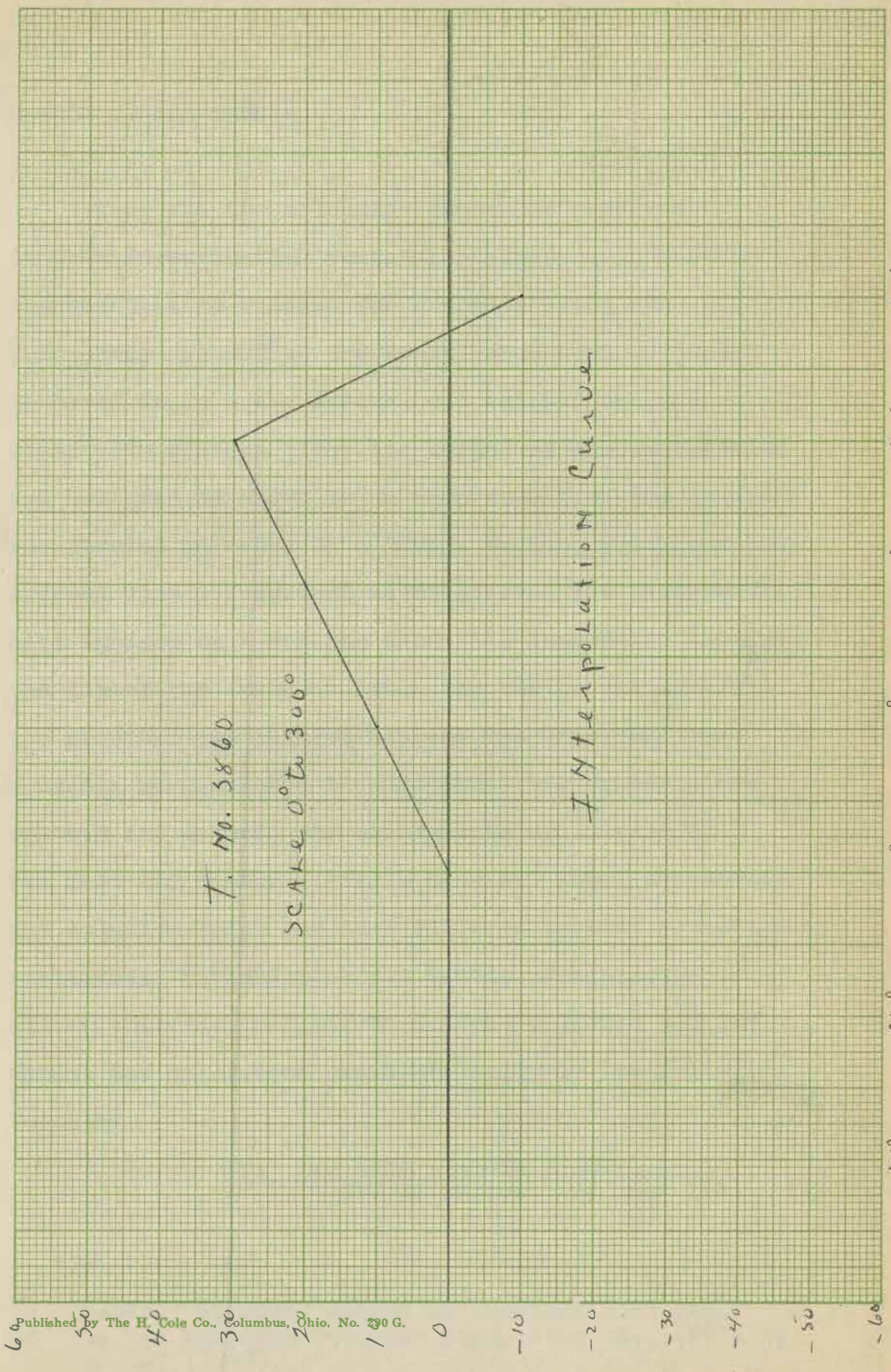
CORRECTION TO READING (DEGREES)



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METHOD OF ANALYSIS:-

Since all the molecular compounds prepared in this investigation contained chlorine, it was thought best to analyze for chlorine using the Pringsheim method[62]. One-tenth gram sample, finely powdered in an agate mortar, was weighed out and mixed with sixteen times its weight of sodium peroxide and 0.1 gram of sugar in an iron crucible. The crucible was floated on water in a 600cc. beaker, which was then covered with a four-inch watch glass. The mixture was next ignited by a red hot iron file introduced through the lip of the beaker. After the fusion was complete the crucible was plunged beneath the water and its contents were allowed to dissolve. The crucible was removed and washed, the washings being allowed to run into the beaker. Nitric acid was added to acidify the solution which was then filtered to remove the carbon particles. The chlorine was lastly precipitated as silver chloride, weighed on a Gooch crucible and the amount was determined gravimetrically by the following formula:

$$\frac{\text{Wt. of AgCl} \times .2474 \times 100}{\text{Wt. of Halide}} = \% \text{ Cl.}$$

62 Scott, "Standard Method of Chemical Analysis," D. Van Nostrand Co., New York, 4th. ed,, Vol. I, p. 147 (1927).

This method gives very accurate results if properly carried out. The chief precautions are: (1) the sample should be thoroughly mixed with sodium peroxide; (2) the iron file should be very hot when introduced into the mixture so as to ignite it with certainty; (3) an iron crucible should be used because a porcelain crucible is liable to break and admit water which will cause a very violent explosion; (4) the fused mass should be allowed to cool somewhat before plunging it into water; (5) the beaker should be well covered during the fusion as splattering is considerable; (6) too large amount of the halide should not be used since the fusion will be too violent, (less than 0.1 gram of picryl chloride-α-naphthol could be used with safety); and (7) during the mixing of the halide care should be taken in preventing moisture from coming in contact with the mixture as ignition may take place instantaneously seriously burning the experimenter.

Usually there are a few carbon particles left in the solution which must be filtered off before the precipitation of the chlorine. Sometimes there is a film of organic matter on the surface after the fusion which indicates that it is incomplete. In cases of this kind the experiment must be repeated.

METHOD OF ANALYSIS OF SUBSTITUTION COMPOUNDS

Since the substitution compounds, isolated in this investigation, do not contain chlorine, analysis was made for nitrogen. The method employed for the determination of nitrogen was that of Kjeldahl as modified by Sisley and David[63]. The method may be briefly summarized as follows: Five-tenths to one gram of the sample was boiled in a Kjeldahl flask by refluxing with 10cc. of alcohol, 5cc. of water and 2-4 grams of sodium hydrosulfite until decolorization, which required from 10 to 15 minutes, took place. After cooling, 10cc. of sulfuric acid were added and the greater part of the alcohol was expelled. By then 5 grams of copper sulfate and 12 cc. of concentrated sulfuric acid were added. The solution was then heated below the boiling point until a blue color was obtained. After diluting to 300cc., 100cc. of NaOH of 36° Baume, 5cc. of 20% sodium sulfide solution and a few pieces of granular zinc were added. The ammonia was distilled over by the use of the ordinary Kjeldahl apparatus into a standard solution of hydrochloric acid. The hydrochloric acid was titrated back against a standard

63 Sisley and David, Bull. Soc. Chim. France 45, 312 (1929)

solution of sodium hydroxide using methyl red as the indicator. Calculations were made by the use of the formula:

$$\frac{\text{Nitrogen} \times \text{cc. of HCl} \times \text{Normality} \times 100}{1000 \times \text{Wt. of Sample}} = \%\text{of N}$$

PART IV

EXPERIMENTAL RESULTS

ADDITION COMPOUNDS OF PICRYL CHLORIDE:-

Sixteen addition compounds of picryl chloride, among which three were prepared for the first time, were isolated in this investigation. The compounds of picryl chloride with (1) naphthalene, (2) fluorene, (3) diphenyl, (4) triphenylmethane, (5) anthracene, (6) α-naphthylamine, (7) dimethylaniline, (8) diphenylamine, (9) carbazole, (10) pyridine, (11) benzene, (12) phenanthrene, and (13) diphenyl methane have been described in the historical part of this thesis. The compounds with picryl chloride and (14) α-naphthol, (15) β-naphthol, and (16) guanidine were new.

TABLE OF THE PHYSICAL PROPERTIES OF THE MOLECULAR COMPOUNDS OF PICRYL CHLORIDE:-

Second Component	Mol. Ratio in Lit.	Mol. Ratio Found	M.P. Lit.	M.P. Obs.	M.P. Cor.	Color and Cryst. Form
1. Naphthalene	1:1	-	91.2°* 94.0 95-96	92.2°	93.1°	Long, yellow needles
2. Fluorene	1:1	-	69-70	69.8	70.2	Orange needles
3. Diphenyl	1:1	1:1	-	78.8	79.4F	Orange-yellow needles
4. Triphenylmethane	1:1	3:2[64]	-	71.8	72.2F	Small, yellow needles
5. Anthracene	1:1	-	141.6	139.6	141.8	Red needles
6. α-Naphthylamine[65]	1:1	-	110-111.5	110.6	111.6	Brown needles
7. Dimethylaniline	1:1	1:1	68	48.2	48.4[66]	Bluish-black needles
8. Diphenylamine	2:1	-	62-66	62.9	63.2	Red needles
9. Carbazole	1:1	-	155	152.4	154.4	Deep-red needles
10. Pyridine	1:1	1:1	138	137.6	138.9	Brown Crystals

Second Component	Mol. Ratio in Lit.	Mol. Ratio Found	M.P. in Lit.	M.P. Obs.	M.P. Cor.	Color and Cryst. Form.
11. Benzene[67]	1:1	-	-	34.4°	34.4°F	Yellow flakes
12. Phenanthrene	1:1	-	88°	86.9	87.9	Long, yellow needles
13. Diphenylmethane	1:1	-	-	78.6	79.6F	Yellow Crystals
14. α-Naphthol[68]	-	1:1	-	122.4	123.0F	Orange needles
15. β-Naphthol[68]	-	1:1	-	103.8	104.4F	Yellow needles
16. Guanidine[69]	-	1:1	-	173.8	177.2F	Yellow Crystals

* The melting point of this compound was reported variously by different investigators.

F Indicates that the melting point was determined for the first time.

64 Analysis of triphenylmethane picryl chloride failed to give either the 1:1 ratio or 3:1 ratio which was announced by Bruni and Ferrari, (Chem. Ztg. 30, 568-69 (1906). Hisey (Thesis, University of Tenn., 1927) stated that he isolated a molecular compound of 2, 4-dinitrochlorobenzene and triphenylmethane having a molecular ratio of 2:3 and melting at 87.9. Wood (Thesis, University of Tenn. 1929) attempted the preparation of the compound prepared by Hisey but with no success. The melting point corresponded to that of one of the components. If a molecular compound of picryl chloride and triphenylmethane can be isolated it is reasonable to believe that a molecular compound of 2, 4-dinitrochlorobenzene and triphenylmethane exists.

Efforts to prepare the compound prepared by Hisey failed. White crystals separated from the alcoholic solution and melted at 85°. They were recrystallized from alcohol and melted at 92°, the melting point of triphenylmethane. A second attempt was made to isolate the compound by allowing the crystallization to go nearly to completion, only a small amount of the solvent being poured off. Two kinds of crystals separated out from the solution. The melting points were not constant; one portion of the crystals melted at 45° and the other portion at 80°, corresponding respectively to the melting points of the two components. Recrystallization resulted in the separation of the two components. Triphenylmethane melted at 92° and 2, 4 dinitrochlorobenzene at 42°. Triphenylmethane being the less soluble of the two components in alcohol separated out first. Also it is less soluble in alcohol than is picryl chloride. If no molecular compound is formed of these two components, triphenylmethane should separate out first. But small yellow needles which melted at 72.2° separated from the alcoholic solution. This indicated that the solid was not a mixture of the two components but a molecular compound. The yellow needles did not resemble those of picryl chloride.

65 Using alcohol as a solvent only a few crystals of the addition compound formed but it crystalized readily from carbon-tetrachloride in a freezing mixture. The addition compound on standing changed into the substitution compound.

66 The melting point as was reported by Lesser, (Ann. 402, 1-51 (1914)), was 68°. The compound was prepared a number of times and the melting point was always 48°. Analysis gave the compound a 1:1 ratio. On standing in moist air Lesser states that the addition compound, being unstable, forms the substitution compound which melts at 212°. All efforts to form a substitution compound failed. The compound on standing in moist air decomposed into its components.

67 The addition compound crystallized in a freezing solution. The compound was very unstable, resolving into its components. When the crystals were just dry the melting point was determined. Efforts to determine the loss of benzene were unsatisfactory due to the instability of the compound.

68 The addition compounds of the naphthols were isolated by using carbontetrachloride as a solvent. An unsuccessful attempt was made to form the substitution compounds of the naphthols by refluxing the α compound in alcohol and the β compound in benzene for ten hours.

69 Picryl chloride-guanidine was formed by using guanidine nitrate as the second component. Analyses indicated that nitric acid was replaced by picryl chloride.

ANALYTICAL RESULTS:-

Picryl chloride-diphenyl: Calculated for chlorine, 1:1 ratio, 7.89%. Found 7.74% and 7.79%.

Picryl chloride-triphenylmethane: Calculated for chlorine 3:2 ratio, 7.89%. Found 7.61% and 7.61%.

Picryl chloride-dimethylaniline: Calculated for chlorine 1:1 ratio, 8.49%. Found 8.57% and 8.52%. (The percent of chlorine was higher here than the theoretical percent probably due to the instability of the compound.)

Picryl chloride-pyridine: Calculated for chlorine 1:1 ratio, 7.87%. Found 7.72 and 7.82%.

Picryl chloride-α-naphthol: Calculated for chlorine, 1:1 ratio, 8.07%. Found 8.08% and 8.14%.

Picryl chloride-β-naphthol: Calculated for chlorine, 1:1 ratio, 8.07%. Found 8.04% and 7.93%.

Picryl chloride-guanidine: Calculated for chlorine, 1:1 ratio, 10.00%. Found 9.94% and 9.89%.

DETERMINATION OF MOLECULAR WEIGHTS OF MOLECULAR COMPOUNDS:-

The method employed to determine the molecular weights of a number of compounds prepared in this investigation was the freezing point method of Beckmann[70]. The method is described in detail by Findlay[71], Getmann[72], Cartledge[73], Walker[74] and others. The determination was carried out in the apparatus shown (Fig.1). The cooling bath consisted of a glass vessel, A, on the top which rested a lid of

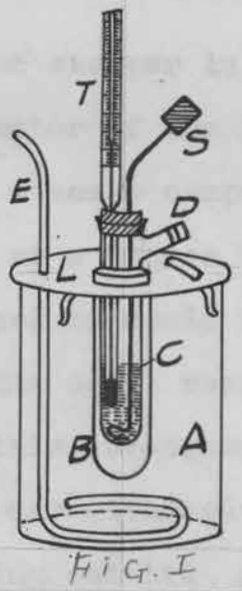


FIG. I

70 Zeit. phys. Chem., 2, 683 (1888)
71 Findlay,"Practical Physical Chem." Longmans, Green and Co., New York, pages 112-122 (1926).
72 Getman, "Outlines of Theoretical Chemistry." John Wiley and Sons, New York, 4th. ed. p. 252-257 (1928).
73 Cartledge, "Inorganic Physical Chem." Ginn and Company, Atlanta, pages 136-137 (1924).
74 Walker, "Introduction to Physical Chemistry," Macmillan and Company, London, 7th. ed. p. 210-212 (1913).

brass, L. Through a hole in the center of the lid there passed a wide glass tube, B, which was fixed in place by means of a rubber stopper; and through another opening in the lid there passed a stirrer, E, by means of which the temperature of the bath could be kept more uniform. The freezing point tube C, which has a side tube D, was supported in the neck of the tube B by a rubber stopper so that the freezing point tube was surrounded by an air mantle. This ensured a slower and more uniform rate of cooling of the liquid.

Through the stopper in the neck of C there passed a thermometer of the Beckmann type. This thermometer had a scale comprising 5° and divided into hundredths of a degree but the quantity of mercury in the column could be varied by means of the mercury in the small reservoir at the top of the scale. By this arrangement the thermometer could be adjusted for use with solvents having widely different freezing points. A stirrer, S, was inserted into the small test tube. To insure freedom of movement and guidance to the stirrer, the latter was made to pass through a short piece of glass tubing inserted through the stopper of the freezing point bulb.

Fifty cubic centimeters of the solvent were measured out in a graduated pipette and placed in the test tube, and the external bath was cooled to a few degrees below the freezing point of the solvent. The temperature of the solvent was lowered by taking it out of the air jacket and immersing it in the freezing mixture until a small amount of the solvent froze. After replacing it in the air jacket, the liquid was stirred vigorously. As there is an invariable undercooling before the solvent is thoroughly mixed, the thermometer would rise during the stirring until it reached the freezing point, after which it remained constant. This constant temperature was then recorded.

The test tube was taken out of the freezing mixture and a weighed quantity of the substance under consideration was introduced through the side arm. The solid was dissolved by stirring, all of the frozen solid being allowed to melt save a small amount. After the tube had been replaced in the air jacket, the temperature was allowed to fall in order that the liquid may become slightly undercooled. When the stirring began, the thermometer rose and remained constant for a short time, then slowly sank. The maximum temperature was recorded and taken as the freezing point of the solution.

Raoult's[75] Law states that," equimolecular quantities of different substances dissolved in equal volumes of the same solvent produce the same depression of freezing point. Since equimolecular q uanities contain the same quanities of molecules, it is evident that the magnitude of depression of the freezing point is dependent upon the number of dissolved units present in the solution." From this law, according to Findlay[76], it is possible to determine the molecular weight of the dissolved substance according to the formula:

$$M = k \frac{w}{dW}$$

where w represents the weight of the substance in grams; W, the weight of the solvent; d, the number of degrees of the observed depression and k, a constant dependent on the solvent used. k indicates the lowering of the freezing point caused by dissolving one gram molecule of the substance in one gram of the solvent. Since only two solvents, benzene and acetic acid, were used the value for k for these is 5120 and 3850 respectively.

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75 Raoult, Compt. rend. 104, 1430 (1887).
76 Findlay, loc. cit.

Findlay[77] listed a number of precautions to which attention was given.

(1) The temperature of the cooling bath must not be too low.

(2) The amount of supercooling should not exceed 0.3° to 0.5°.

(3) Stirring should not be too rapid and should be as uniform as possible.

(4) The thermometer should always be tapped before taking a reading.

(5) If acetic acid is used as solvent special precautions must be used to prevent access of moisture from the air.

The above method can only be employed when the solute does not form an isomorphous mixture with the solid solvent, i.e. only when the solvent crys allizes out pure. Abnormal molecular weights are obtained when molecules combine to form a larger molecule, i.e. associate in solution; or, when a molecule breaks down to form smaller molecules. If association takes place the molecular weight is much greater than that calculated from the chemical formula of the substance, or, if dissociation takes place the molecular weight is smaller than that calculated from the chemical formula.

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77 Findlay, loc. cit.

Nearly all salts, bases and acids, which ionize in aqueous solution, give abnormal molecular weights.

According to Findlay[78], the degree of dissociation may be calculated in the following manner: If α represents the degree of dissociation, and if n represents the number of dissociated molecules (ions) formed from each molecule of solute, then the relative increase in the number of molecules (or molecules plus ions) in the solution will be as $1:1+(n-1)\alpha$. d_o and d_t represent the observed and the theoretical (on the assumption of no dissociation) depressions, whence

$$\frac{d_o}{d_t} = \frac{1+(n-1)\alpha}{1}$$

$$\text{or,} \quad d_o = d_t(1+(n-1)\alpha)$$

$$d_o = d_t - d_t\,\alpha(n-1)$$

$$d_t\,\alpha(n-1) = d_o - d_t$$

$$\alpha = \frac{d_o - d_t}{d_t(n-1)}$$

78 Findlay, loc. cit.

If M_t represents the molecular weight calculated from the observed depression and M_o the molecular weight calculated from the chemical formula,

it follows that-------

$$\alpha = \frac{M_o - M_t}{M_t(n-1)}$$

TABULAR RESULTS OF DETERMINATION OF MOLECULAR WEIGHTS:-

TABLE NO. I

Second Component	Amt. of Solvent	Grams of Solute (Two Determinations)	Depression of Freezing Point
1. α-Naphthol	50cc.	0.4071 and 0.3125 grs.	0.159 and 0.123°
2. β-Naphthol	50	0.2617 " 0.2231 "	0.119 " 0.109
3. p-Toluidine-o-nitrophenol	50 A	1.3964 " 0.8624 "	0.712 " 0.667
4. p-toluidine-p-nitrotoluene	50 A	1.1630 " 0.9361 "	0.827 " 0.666
5. Guanidine	50	0.1098 " 0.0936 "	0.038 " 0.035
6. Phenanthrene	50	0.4216 " 0.2164 "	0.182 " 0.104
7. Dimethylaniline	50	0.1857 " 0.1113 "	0.097 " 0.055

A. These compounds include both the first and second components.

TABULAR RESULTS OF DETERMINATION OF MOLECULAR WEIGHTS:-

TABLE NO. II

Second Component	Mol. Wt. From Chem. Formula	Mol. Wt. Found	α or Degree of Dissociation
1. α-Naphthol	439.56	298.6 and 275.9[79]	.472 and .557[80]
2. β-Naphthol	439.56	261.8 " 236.7	.641 " .837
3. p-Toluidine-p-nitrophenol[81]	246.30	180.7 " 150.6	.346 " .635
4. p-Toluidine-p-nitrotoluene[81]	244.18	160.2 " 146.1	.524 " . 658
5. Guanidine[82]	354.62	206.5 " 189.6	.717 " .870
6. Phenanthrene	473.66	263.7 " 246.7	.790 " .923
7. Dimethylaniline	419.62	232.1 " 213.2	.889 " .969

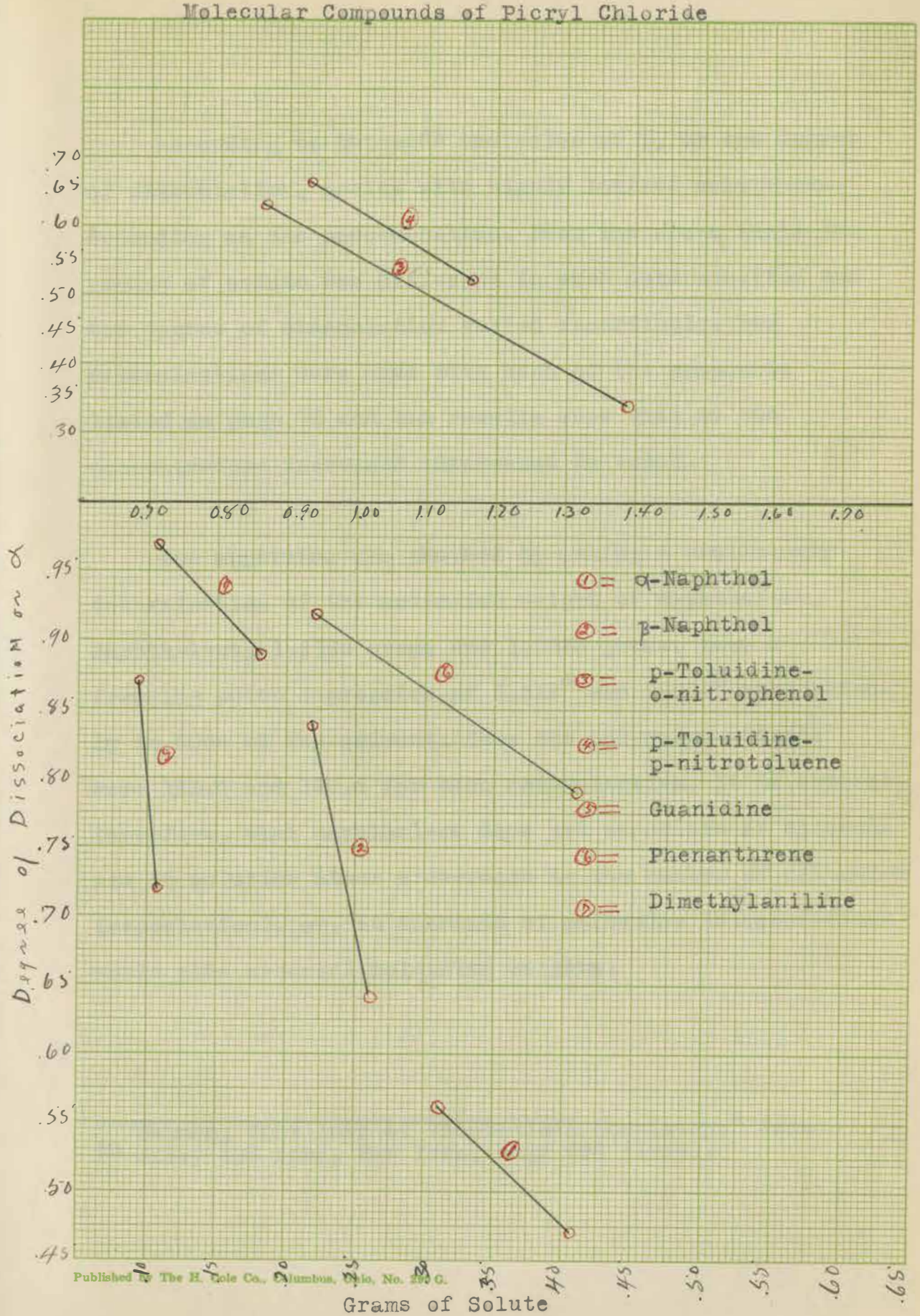
79 The molecular weights found and the degree of dissociation are arranged according to the amount of solute used.

80 Since the molecular ratio of the components in the above compounds is 1:1, it is assumed that n is equal to 2 (n being the number of dissociation molecules formed from each molecule of the solute.)

81 These compounds were prepared by C. R. Alexander, (Thesis, University of Tennessee, 1930). Both components are given.

82 The addition compound of picryl chloride and guanidine was insoluble in benzene; the solvent was acetic acid.

Degree of Dissociation Curve of Molecular Compounds of Picryl Chloride



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According to Getman[83] the value of α, or the degree of dissociation, varies with highly ionized substances depending on the concentration. From the above table the amount of solute was different in each determination and the degree of dissociation varied accordingly. Two determinations were made with each of the compounds listed on page 76 and the results show that as the concentration increased α decreased in value.

The apparatus was checked by making a preliminary determination of the molecular weight of naphthalene. Naphthalene, 1.4160 grams and 1.0835 grams, gave a freezing point depression of 1.314° and 1.024° respectively in 50cc of the solvent. Thus the molecular weights were 125.6 and 123.4 for each determination. It is evident, therefore, that naphthalene does not associate or dissociate in solution since a decrease in the number of molecules (association), or, an increase of molecules (dissociation) would give abnormal molecular weights.

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83 Getman, "Outlines of Theoretical Chemistry," John Wiley and Sons, New York, page 482 (1929).

POSSIBLE MOLECULAR COMPOUNDS OF PICRYL CHLORIDE NOT ISOLATED

It is sometimes very difficult to isolate a molecular compound from its solution. This may be either due to the fact (1) that the molecular compound is a liquid at ordinary temperatures or (2) that the affinity is so slight between the two molecules that the molecular compound exists only in solution. Since the color of the molecular compound is usually deeper than that of either component, one can predict the formation of molecular compounds by this property. Again, the existence of molecular compounds may be predicted by the freezing point methods.

It is assumed that the following compounds exist in solution: (1) picryl chloride-methylaniline, (2) picryl chloride-p-aminophenol, and (3) picryl chloride-m-toluidine. When picryl chloride and methylaniline are boiled in alcohol a deep red color forms. The solution deposits a few red crystals which correspond to the substitution compound. By repeating the experiment in a freezing mixture bright-red needles formed, but when placed in the air they readily decomposed. The needles were placed in a tightly stoppered bottle and

were left to remain in the freezing mixture, but when taken from the mixture they formed the substitution compound picrylmethylaniline. Similarly, when picryl chloride and p-aminophenol were boiled in alcohol a dark red color appeared. At the temperature of the freezing mixture, scarlet crystals were formed which changed readily to the substitution compound, picryl-p-aminophenol. Efforts to determine the melting point of the scarlet crystals were unsatisfactory. The alcoholic solution of picryl chloride and m-toluidine had at first a dark color indicating the possible formation of a molecular compound, but the solution soon changed to a light yellow with the formation of the substitution compound.

POSITION OF THE CHLORINE ATOM IN THE MOLECULAR COMPOUNDS OF PICRYL CHLORIDE

It is possible to have either true molecular compounds of picryl chloride and amines or to have the hydrochlorides of the substituted amines. Both explanations are possible according to the analyses of these molecular compounds. But the compound's properties depend upon the formula which it possesses.

If the addition compounds of picryl chloride are true molecular compounds, the chlorine atom should be firmly bound to the nucleus and not be precipitated by silver nitrate even in alcoholic solution. If the chlorine atom is attached to the nitrogen atom loosly, then it should be precipitated by silver nitrate in cold alcoholic solution.

Kamm[84] gives the following scheme of determining the attachment of the halogen atom to the nucleus:

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84 Kamm, Qualitative Organic Analysis, Edition I, page 40, John Wiley and Sons (1922).

(1). Water soluble compounds containing ionizable halogen will react instantaneously, even with aqueous silver nitrate.

(2). Water insoluble acyl halides, tertiary halogen compounds, etc., react instantaneously with alcoholic silver nitrate.

(3). Primary and secondary halogen compounds in the aliphatic series, aromatic compounds with halogen in the side chain, react slowly with alcoholic silver nitrate but fairly rapidly on heating.

(4). Aromatic compounds containing halogen in the ring do not react even upon heating.

Therefore, if the chlorine atom is attached to the amino group, it should be precipitated readily by alcoholic silver nitrate, but if it is in the ring, as in the true molecular compounds, it should not react at all.

Only the pyridine compound prepared in this investigation gave a precipitate with silver nitrate. The other compounds were boiled with alcoholic silver nitrate but

no precipitation resulted. This indicated that the chlorine atom is attached to the nucleus in all the compounds prepared with the exception of that of pyridine.

A DISCUSSION OF THE MOLECULAR COMPOUND OF PYRIDINE AND PICRYL CHLORIDE:-

As stated previously, Wedekind[85] isolated a molecular compound of picryl chloride and pyridine, having a molecular ratio of 1:1, from benzene solutions of the two components. The same compound was isolated in this investigation from a benzene solution. An attempt to form the compound from alcoholic solutions failed. Recrystallization resulted in the formation of the substitution compound. Hodges[86] stated that Wedekind's compound is an intermediate stage in the formation of picryl pyridinium chloride, having a molecular ratio of 2:1 and readily ionizing to form picryl pyridinium picrate. Hodges' exact method of procedure was used in an attempt to prepare his compound but only the compound isolated by Wedekind could be prepared.

The constitution of this compound must be different from that of the other molecular compounds prepared in this investigation. It gives a precipitate with alcoholic silver nitrate in the cold, whereas none of the other

85 Wedekind, loc. cit.
86 Hodges, loc. cit.

compounds reacted similarly. Analysis by the sodium peroxide fusion method gave the amount of chlorine as 7.72%, and analysis of chlorine by precipitation in an alcoholic solution of silver nitrate gave 7.60% chlorine. Since the amount of chlorine determined by both methods is the same, it is presumed that the chlorine atom is ionized resulting in the formation by rearrangement of a complex salt[87].

Buehler, Hisey and Wood, J. Am. Chem. Soc. 52, 87 1939 (1930).

MOLECULAR COMPOUNDS AS INTERMEDIATES IN SUBSTITUTION REACTIONS:-

It is the idea of Kekule[88], Michael[89], Thiele[90], and Armstrong[91] that all substitution reactions are preceded by the formation of intermediate addition compounds. An attempt was made to bring about the formation of the substitution compounds from the molecular compounds prepared in this investigation. The compounds were refluxed in alcohol for about ten hours.

As stated previously, the molecular compounds of α-naphthol, β-naphthol and dimethylaniline were refluxed for about ten hours and the substitution compounds did not form. In general the results were negative with hydrocarbons and phenols.

Some of the molecular compounds with amines formed the substitution compounds readily, splitting off hydrogen

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88 Kekule, Organische Chemie, Vol. II, p. 730 et seq., Ferd. Enke., (1887)

89 See Henrich, Theories of Org. Chem., p. 569-570 John Wiley and Sons, American Edition (1920)

90 See Henrich, Theories of Org. Chem., p. 33-75 John Wiley and Sons.

91 Armstrong, J. Chem. Soc. 51, 258 (1887)

chloride. Picryl chloride- α-naphthylamine needed no refluxing, changing in the air to picryl- α-naphthylamine. The tendency toward substitution was so great in the case of picryl chloride and β-naphthylamine that the molecular compound could not be isolated. The color of the components in carbon tetrachloride indicated an addition compound, but this deep color changed instantaneously to a light red.

It might be stated that the tendency of the molecular compounds of picryl chloride to form the substitution compounds is much more pronounced among amines than hydrocarbons and phenols.

SUBSTITUTION COMPOUNDS OF PICRYL CHLORIDE:-

Thirteen substitution compounds were prepared in this investigation, one of which was prepared for the first time by the method employed. The substitution compounds of picryl chloride with (1) α-naphthylamine, (2) β-naphthylamine, (3) aniline, (4) methylaniline, (5) o-toluidine, (6) p-toluidine, (7) o-phenylenediamine, (8) p-aminophenol, (9) diethylamine, (10) xylidine, (11) p-nitraniline, and (12) m-toluidine were prepared by earlier investigators and described in the historical part of this thesis. The substitution compound of picryl chloride with (13) benzidine was prepared for the first time.

TABLE OF PHYSICAL PROPERTIES OF SUBSTITUTION COMPOUNDS OF PICRYL CHLORICE:-

Compound	M.P. in Lit.	M.P. Obs.	M.P. Cor.	Color and Cryst. form
1. Picryl-α-naphthylamine	197-198°[92]	193.4°	197.1°	Orange-red crystals
2. Picryl-β-naphthylamine	231-234[93]	227.9	232.3	Red crystals
3. Picrylaniline	177.5 [94]	174.9	177.7	Yellow crystals
4. Picrylmethylaniline	108-110[95]	107.8	109.0	Red crystals
5. Picryl-o-toluidine	164[96]	160.2	163.2	Orange prisms.
6. Picryl-p-toluidine	163-165[97]	159.9	162.9	Orange needles
7. Picryl-o-phenylenediamine	177-178[98]	173.2	176.3	Dark-brown crystals
8. Picryl-p-aminophenol	172-173[99]	173.4	177.0	Orange flakes
9. Picryldiethylamine	163-164[100]	162.6	165.3	Orange leaflets
10. Picryl-xylidine	158[101]	154.2	156.8	Deep orange red needles
11. Picryl-p-nitraniline	214-216[102]	213.9	217.2	Fine yellow needles
12. Picryl-m-toluidine	126[103] 130 163	128.2	131.2	Yellow Crystals

Compound	M.P. in Lit.	M. P. Obs.	M.P. Cor.	Color and Cryst. Form
13. Picrylbenzidine -		251.9	259.1	Reddish Brown Crystals

92 Sudborough and Picton, J. Chem. Soc. 89, 594 (1906).
93 Bamberger and Muller, Ber. 33, 110-113 (1900).
94 Turpin, J. Chem. Soc. 59, 714 (1891).
95 Busch and Pungs, J. prakt. Chem. 79, II, 546-554 (1909).
96 Kehrmann, Ramm and Schmajewski, Mit. Helv, Chim. Acta, 2, 379 (1921).
97 Busch and Pungs, loc. cit.
98 Leeman and Grandmaugin, Ber. 41, 1305 (1908).
99 Wedekind, Ber. 31, 1679 (1898).
100 Romburg, Rec. trav. chim. 4, 191 (1885).
101 Busch and Pungs, loc. cit.
102 Austen, Ber. 7, 1248 (1874).
103 Leeman and Grandmaugin, loc. cit. As stated previously, Leeman and Grandmaugin prepared picryl-m-toluidine which melted at 126°. Busch (J. Chem. Soc. 96, 564 1909) stated that he formed two modifications of picryl-m-toluidine, a mixture of yellow prisms which melted at 130° and orange red needles which melted at 163°. Only one modification could be isolated in this investigation, the one corresponding to Busch's compound which melted at 131.2°.

ANALYSIS OF PICRYL BENZIDINE:-

Since picryl benzidine does not contain chlorine analysis was made for nitrogen using the modified Kjeldahl method which has been previously discussed.

Picryl benzidine: Calculated for nitrogen, 15.83%. Found 15.85% and 15.71%.

NOTE ON PICRYL CHLORIDE:-

Hisey[104] stated that 2, 4-dinitrochlorobenzene is a mild skin irritant, since continued contact with it produces blisters accompanied by intense itching. Picryl chloride produces the same effect as the compound described by Hisey. After a week no injurious effects were noticed, but after two weeks deep blisters formed under the epidermis and the itching was intense until after a few days when the epidermis peeled off. If the chloride comes in contact with any other portion of the body the pain is more severe than that of the hands. Furthermore, picryl chloride colors the skin a deep yellow and cannot be entirely removed by any solvent.

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104 Hisey, Alan, Thesis, University of Tennessee, p. 40 (1927).

PART V

THEORETICAL DISCUSSION

I. Theories of Formation of Molecular Compounds.

Many theories have been advanced relative to the possible formation of molecular compounds. These theories, however, do not, in all cases, explain satisfactorily the various forms of linkage of molecular compounds. Each theory may be applicable to a special case, but as yet, no one theory can be applied to the entire field of molecular compounds. These theories are divided into three general divisions; (1) those based on the idea of partial valence, (2) those based on principal valence, and (3) the electronic theories of valence. The first theory is supported by Thiele, Morris, Werner, and Pfeiffer; the second by Kendall, and Sudborough; the third by Lewis, Sidgwick and Bennett and Willis. A brief discussion of each theory will be given.

A. Theories of Partial Valence.

Thiele[105], in 1899, stated that the source of

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105 Thiele, J. Chem. Soc. Abs. 76, I, 554 (1899); Ann. 306, 87-142 (1899).

additive capacity of a compound was due to the incomplete absorption of the combining energy of the double bond linkage. According to the above theory this left a partial valency or residual affinity on each carbon atom. Thiele's idea may be illustrated by the examples shown in Fig. A and Fig. B:

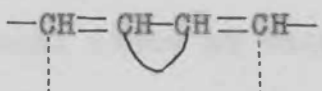


Fig. A

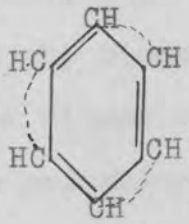


Fig. B

In chains of double bond type as in Fig. A, the carbon atoms near the center become inactive due to mutual compensation. The carbon atoms at the end remain free and the addition takes place at those points. Thiele's idea is also applicable[106] to Kekule's formula for benzene as is shown in Fig. B. The conjugated system of the benzene ring exerts its additive possibilities by the exercising of the partial valencies.

Norris[107] suggested that the formation of molecular compounds was due to the existing latent affinity or residual energy which resides in each atom of the components. He stated that every element contains a

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106 Stewart's "Recent Advances in Organic Chemistry", Longmanns, Green and Co., New York, 4th. Ed. 1920, p. 10-13.

107 Norris, J. Am. Chem. Soc. 38, 702 (1916).

definite amount of chemical energy which undergoes partial transformation when the element enters in combination with another element. The amount of chemical energy in the resulting compound is determined by the amount of energy transformed in its formation. This residual energy, which is still present in the atoms, makes it possible for the molecule to unite either with additional atoms or with molecules to form molecular compounds.

Werner[108] regarded the molecular compounds of nitro-bodies and hydrocarbons as being formed by the saturation of the residual affinity between the nitro groups and the unsaturated carbon atoms. The following formula represents his type of linkage:

$$R(NO_2)_r \ldots\ldots\ldots\ldots\ldots C_n H_m$$

Pfeiffer[109] supported the views of Werner as to the formation of molecular compounds of nitro-bodies with amines, phenols, and phenol ethers. He contended

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108 Werner, Ber. 42, 4324 (1909).
109 Pfeiffer, "Organische Molekulverbindungen," Ferdinand Enke, Stuttgart, 1922, 2nd. Ed. p. 221.

that the color of the molecular compounds is deepened by the introduction of color groups such as "NH_2" or "OH", and if the linkage is through these groups the color properties are lost. Since the color of molecular compounds of nitro-bodies with amines is so pronounced he concluded that the affinity must therefore come from the unsaturated carbon atoms of the nucleus. Werner[110] assumed that the collective affinity of the unsaturated carbon atoms is exerted by a single atom in each component. Pfeiffer differed from Werner's views in that he believed that the collective energy of the carbon atoms is radiated through the "polyatomic valence field" with each molecule as a center.

B. Theories of Principal Valence.

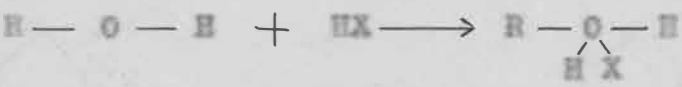
Kendall[111] in his attempt to explain the formation of molecular compounds advanced the oxonium theory. According to his theory, molecular compounds are formed only when the acidic strengths of the two components are widely different. To illustrate, a strong acid and a weak phenol will probably form a compound, but a weak acid and a strong phenol will probably not. He stated that a true

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110 Werner, loc. cit.

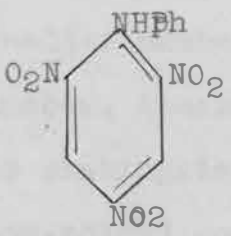
111 Kendall, J. Am. Chem. Soc. 36, 1222, 1722, 2498 (1914); 37, 149 (1915); 38, 1309 (1916).

oxonium salt is formed as a result of the molecular neutralisation which may be represented by the equation:

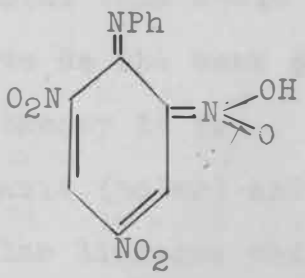


In the case of phenols he suggested that a tautomeric quinoidal structure is possible, and that the molecular compound is formed through the phenolic oxygen which is potentially quadrivalent.

Sudborough and Picton[112] have suggested that the formation of a molecular compound was due to a shifting of the benzenoid structure to the quinoidal form as is indicated below:



Benzenoid



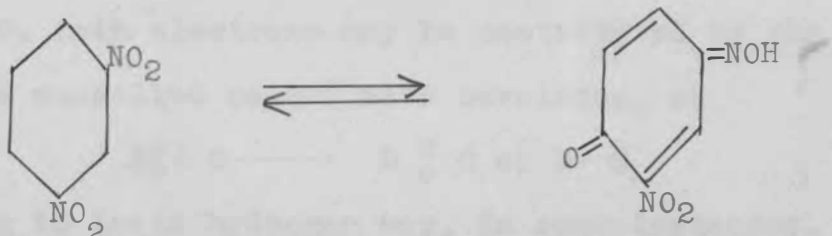
Quinoid

The shift to the quinoidal form, it was thought, was responsible for the intensification of color which usually accompanies the formation of molecular compounds.

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112 Sudborough and Picton, J. Chem. Soc. 89, 1, 533 (1906).

Buehler and Heap[113] followed the suggestion of Sudborough and Picton[114] and gave to the nitro-body a quinoidal structure with the formation of a "NOH" group which is represented as follows:



C. The Electronic Conception of Valence.

Lewis[115], in 1916, in his discussion of the atom and the molecule, stated that the cause of chemical combination was the redistribution of the electrons among the atoms causing a more stable combination. He maintained that an electron could be shared by two atoms in such a way as to increase the stability of both. This would enable a smaller number of electrons to do the work of a larger number. According to Lewis' theory it is possible to distinguish between inorganic (polar) and organic (non-polar) compounds. Non-polar linkages which are due to the sharing of electrons arise in one or the other of two ways:

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113 Buehler and Heap, J. Am. Chem. Soc. 48, 3168 (1926).
114 Sudborough and Picton, loc. cit.
115 Lewis, J. Am. Chem. Soc. 38, 762 (1916).

1. One electron may be contributed by each atom, the so-called normal covalency, as

$$D^{\circ} + {}_{\circ}C \longrightarrow D \overset{\circ}{\underset{\circ}{}} C \text{ or } D{-}C$$

2. Both electrons may be contributed by the same atom, the so-called co-ordinate covalency, as

$$D^{\circ}_{\circ} + C \longrightarrow D \overset{\circ}{\underset{\circ}{}} C \text{ or } D{-}C$$

According to Lewis hydrogen may, in some instances, be bivalent. It is possible for hydrogen to possess the two types of covalencies simultaneously.

Sidgwick[116] has applied to the Werner complexes the ideas of Lewis. He found that these ideas could be successfully used in explaining the existence of these complexes.

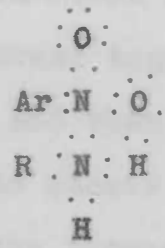
Bennett and Willis[117] have proposed formulas for the compounds formed between nitro compounds and amines and hydrocarbons. These investigators assumed that the union takes place by means of co-valent linkages and that the nitro group is the point of attachment in

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116 Sidgwick, "The Electronic Theory of Valence," Oxford University Press, 1st. Ed. (1929) p. 116.

117 Bennett and Willis, J. Chem Soc. 256 (1929).

the nitro compound. The following scheme represents an amine nitro compound, the amine being the donor and the nitro compound the acceptor:



II. Theories that Molecular Compounds are Intermediates in the Formation of Substitution Compounds.

The idea that reactions between organic compounds are due to an attraction between molecules resulting in an initial combination is not new. Kekule[118], in 1867, stated that "in any chemical action the two reacting molecules are first drawn together by mutual exercise of chemical affinity and then ultimately become attached to each other. In this closer association, individual atomic attractions make themselves felt, with the result that atoms which had previously been present in two different molecules come into very close proximity. Such arrangement may finally lead to the disruption of the whole complex and the formation of entirely new molecules."

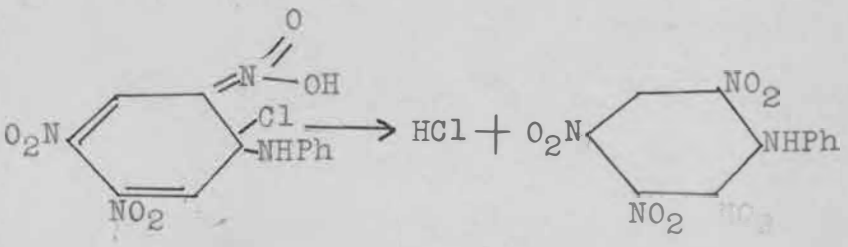
Pfeiffer[119] stated that addition compounds are intermediates to the formation of substitution compounds. Reddelien[120] extended Pfeiffer's views on the >C=O group to substances containing such groups as >C=N— and —N=N—

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118 Kekule, "Organische Chemie," Ferdinand Enke, Stuttgart, Vol. II, p. 730 (1867).
119 Pfeiffer, loc. cit.
120 Reddelien, J. pr. Chem. 91, 213 (1915).

Guye[121] and also Schmidlin and Lang[122] stated that substitution reactions are preceded by the formation of addition compounds. The latter investigators studied the reactions of various phenols with acetone in the presence of a condensing agent without the use of heat. By this method they prepared addition compounds which passed readily into the corresponding condensation products.

Sudborough and Picton[123] found that the addition compounds of picryl chloride with α and β-naphthylamines readily lost hydrogen chloride and formed the substitution products. The reaction could not be reversed by boiling the compounds with hydrochloric acid. They represented the addition compound by giving it the quinoid structure. This structure readily loses hydrogen chloride and changes into the condensation product, thus:



121 Guye, J. chim. phys. 8, 119, 189 (1910).
122 Schmidlin and Lang, Ber. 43, 2808 (1910).
123 Sudborough and Picton, J. Chem Soc. 89, 583 (1906).

Guia, Marcellino and Curti[124] isolated a fairly stable addition compound of trinitroanisole and piperidine from alcoholic solution. The substitution compound, picryl piperidine, was formed by boiling the addition compound in alcohol containing sodium carbonate. These investigators followed the suggestion of Sudborough and Picton[124] and represented the addition compound as having a quinoidal structure.

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124 Guia, Marcellino and Curti, Gaz. 50, 300 (1920).
125 Sudborough and Picton, loc. cit.

III. Application of the Theories to the Compounds Prepared.

The compounds prepared in this investigation had a one-to-one ratio which can be best explained upon the basis of a union of a co-valent type between atoms. Also, according to Bennett and Willis[126], the color of the molecular compounds indicates this type of combination.

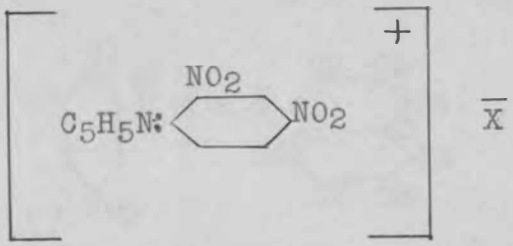
The low melting points of the molecular compounds indicate a loose linkage[127], which is additional evidence in support of the electronic conception of combination. In most cases the melting point of the compound was lower than that of either component.

According to Alexander[128] the number of "NO_2" groups seems to influence compound formation. His idea is borne out in this investigation. The literature search indicated fifty-one addition compounds. Three new compounds were isolated in this investigation making a total of fifty-

126 Bennett and Willis, loc. cit. p. 256.
127 Sidgwick, loc. cit.p105.
128 Alexander, C. R. Thesis, University Tennessee (1930).

four known molecular compounds of picryl chloride. Again, the large number of addition compounds of picric acid[129] gives additional evidence in support of the above idea.

Buehler, Hisey and Wood[130] stated that 2,4-dinitrochloro- and 2,4-dinitrobromobenzenes formed with pyridine an addition compound of temporary existence only. Rearrangement formed a complex salt, the halide atoms being quantitatively precipitated with silver nitrate. The following scheme was used to represent this compound:



The compound of picryl chloride and pyridine supported the theory advanced by these investigators. Since the chlorine was precipitated by silver nitrate, it is evident that the complex salt ionizes readily in solution.

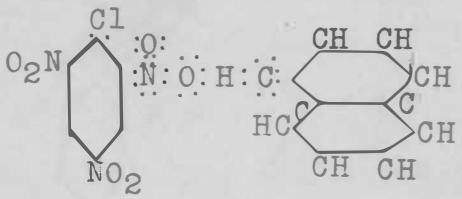
In this investigation molecular compounds of picryl chloride with hydrocarbons, amines, and phenols were prepared. Of the theories set forth, in an attempt to explain the linkage of molecular compounds, the most

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129 Lowery, J. Clyde, Thesis, University Tennessee (1926).
130 Buehler, Hisey and Wood, J. Am. Chem. Soc. 52, 1943 (1930).

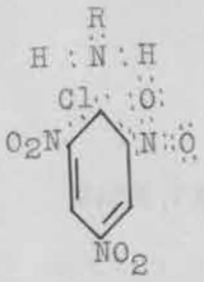
applicable is the electronic. As representatives of these classes of compounds, naphthalene, α-naphthylamine and α-naphthol formed the most stable addition compounds.

An attempt will be made to represent the linkage of the above compounds by means of the co-ordinate covalence idea. The formula below represents the type of linkage between picryl chloride and naphthalene:

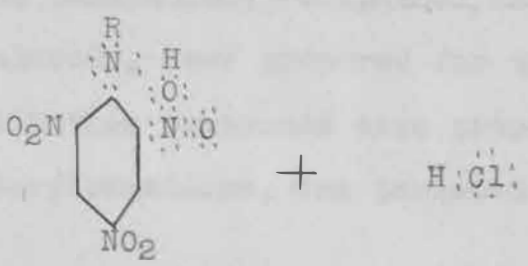


The hydrocarbon compound is the donor and the nitro compound is the acceptor. The addition compounds with hydrocarbons did not lose hydrogen chloride to form the substitution compound as in the case of the amines. An attempt was made to form the substitution compounds by refluxing in alcohol but the results were negative.

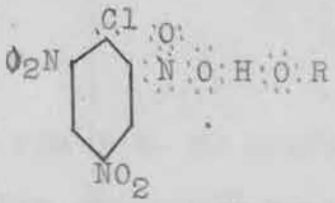
The type of linkage of amines with picryl chloride may be illustrated thus:



The amine is the donor and the nitro compound is the acceptor. The above complex was not stable with the more basic amines due to the fact that chlorine was eliminated with one of the hydrogens of the amino group. The following scheme represents the formation of the substitution compound:



The type of linkage of phenols may be represented by the following complex arrangement:



PART VI

SUMMARY

1. The literature search revealed fifty-one molecular compounds and seventy-three substitution compounds of picryl chloride. A total of sixteen addition compounds was isolated in this investigation. Three of these, α-naphthol, β-naphthol, and guanidine with picryl chloride, were prepared for the first time. Thirteen substitution compounds were prepared and of these, one, picrylbenzidine, was isolated for the first time.

2. The compounds were analyzed for chlorine using the sodium peroxide fusion method. The substitution compound was analyzed for nitrogen using the modified Kjeldahl method.

3. An endeavor was made to determine the molecular weights of some of the compounds by the freezing point method. The compounds dissociated in solution, the degree of dissociation decreasing as the concentration increased.

4. The theories that have been advanced for the

formation of molecular compounds were discussed.

5. Electronic formulas were proposed for the linkage of hydrocarbons, amines, and phenols with picryl chloride.

ACKNOWLEDGEMENT

In conclusion, I wish to express my appreciation to Dr. Calvin A. Buehler for his guidance and helpful suggestions during the preparation of this thesis.