# THE PREPARATION OF 2,4,6-TRINITRO-TOLYL-3-METHYL NITRAMINE FROM THE WASTE LIQUOR OBTAINED IN THE PURIFICATION OF T.N.T.

A Thesis

Submitted to

The Faculty of Graduate Studies and Research
of McGill University
in partial fulfilment of the
requirements for the Degree of
Master of Science

Roland Paquette

McGill University April 1943

The author takes pleasure in expressing his thanks

to

Dr. J.H. Ross and Dr. R. Boyer
for invaluable advice and continued
encouragement throughout the duration
of this investigation

National Research Council of Canada
for the award of a Studentship

Dr. Gordon Findlay
and
Defence Industries Ltd.,
McMasterville, Que.,
for the supply of raw material.

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GENERAL INTRODUCTION

# SUMMARY

Optimum conditions were found for amination of the sodium dinitrotolyl-3-sulphonates, dissolved in the spent liquor from the purification of trinitrotoluene by the sodium sulphite process. With methylamine as reagent, one ton of crude trinitrotoluene yields 61.2 lbs. of dinitro-3-N-methyl toluidines.

The nitration of the dinitro-3-N-methyltoluidines by nitric acid and mixed acids has been investigated. The reaction conditions for optimum yield in these various nitrating agents have been set. According to one of these processes, one ton of crude trinitrotoluene would give 61.3 lbs. of m-methyl-tetryl.

# GENERAL INTRODUCTION

The industrial preparation of $\alpha$-trinitrotoluene involves a loss of 20% of the theoretical due to oxidation of the starting material, and to formation of isomers. The oxidation products are mainly CO, $CO_2$, dinitrocresols, di-, tri- and hydroxybenzoic acid, and account for 15% of the loss. The five isomers of $\alpha$-trinitrotoluene represent therefore 5% of the loss and can be transformed into a useful explosive.

The extraction of the unsymmetrical trinitrotoluenes from the crude nitration products is done by treating the crude trinitrotoluene with a solution of sodium sulphite, which dissolves the isomerides as sodium dinitrotolyl-3-sulphonates. At present, sulphite liquors resulting from purification are discarded, but amination of these sulphonates and subsequent nitration of the resulting toluidines give rise to the explosive 2,4,6-trinitrotolyl-3-methylnitramine.

It is not the purpose of the investigation to introduce 2,4,6-trinitrotolyl-3-methylnitramine (m-Methyltetryl) as a new explosive. The justification of the reseach results from the fact that since the raw material is at present a total loss to the explosives industry, it would be possible to produce an explosive of the tetryl class at a low cost.

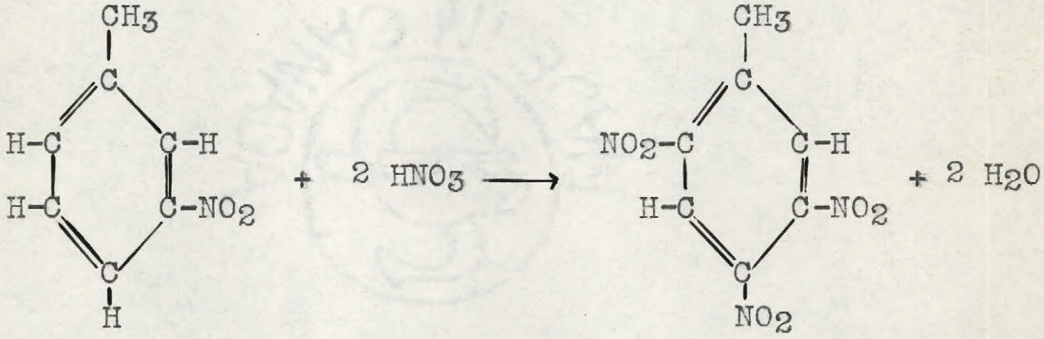
It must be noted that this work was undertaken prior to the publication of "The Chemistry of Powder and Explosives" by T.L. Davis.

# HISTORICAL INTRODUCTION

Although synthesized for the first time by Wilbrand (1) in 1868, trinitrotoluene (TNT) was not immediately used as an explosive. Hausserman, (2) in a paper published in 1891, states that trinitrotoluene, with all the properties of a high explosive, is much less dangerous than picric acid, as powerful as dinitrobenzene, and can be prepared very easily. It was only in 1901 that the commercial production of trinitrotoluene (3) began in Germany. In Great Britain, the trinitrated toluene was accepted as a useful explosive in 1910 (4) but its production was rather small until the beginning of the last World War. It was soon found by the Research Department of the Woolwich Arsenal, G.B., that a material of high setting point was necessary to produce a trinitrotoluene that could be made and used without danger.

Up to 1916 the purification of crude trinitrotoluene was carried out by means of a crystallization process. The crude material was crystallized from alcohol or a mixture of alcohol and benzene. This process gives a very pure product but it is necessarily elaborate, requires considerable plant and the fire hazard is very great.

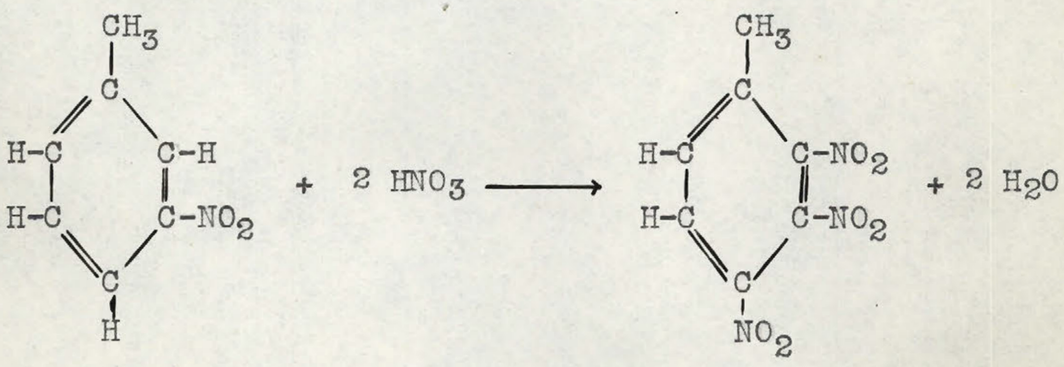
Crystallization from alcohol eliminated from the crude trinitrotoluene the unsymmetrical isomers plus a small amount of dinitrotoluene. It was known since the synthesis of the 2,4,6-trinitrotoluene that six isomers were theoretically possible but it was only in 1868 that Beilstein and Kuhlberg (5) synthesized the 3,4,6 isomer (II) by nitration of the meta nitrotoluene (I).



I

II

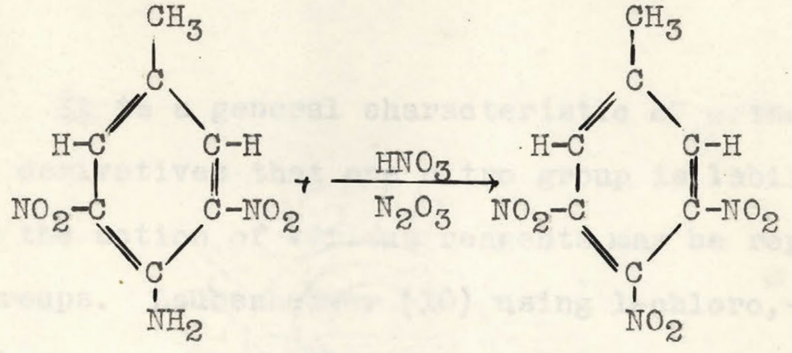
In repeating such a nitration Hepp (6) obtained a mixture of 3,4,6- or γ-trinitrotoluene (II) and 2,3,4- or β - trinitrotoluene (III).



I

III

The other three isomers were synthesized by Korner and Contardi. These authors succeeded, by oxidation of the corresponding dinitrotoluidines, in preparing the 3,4,5- or δ-trinitrotoluene (V) in 1914 (7), the 2,3,5- or ε-trinitrotoluene (VII) in 1915 (8) and the 2,3,6- or η-trinitrotoluene (IX) in 1916 (9).



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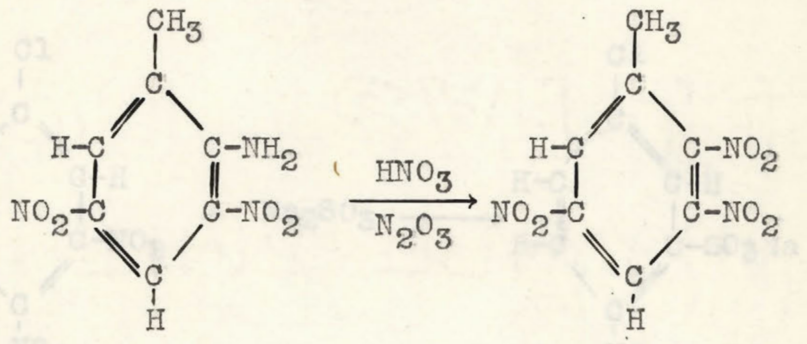

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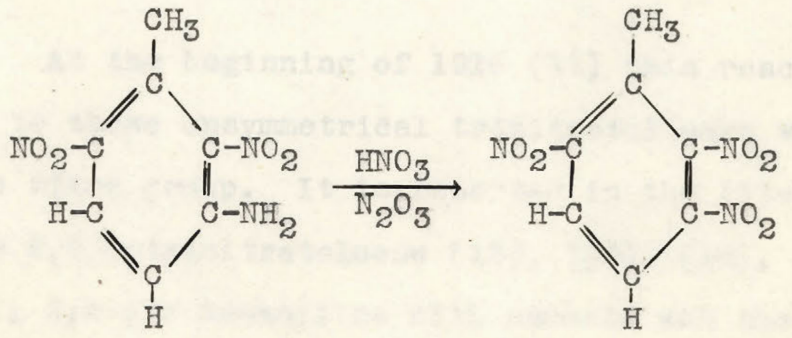
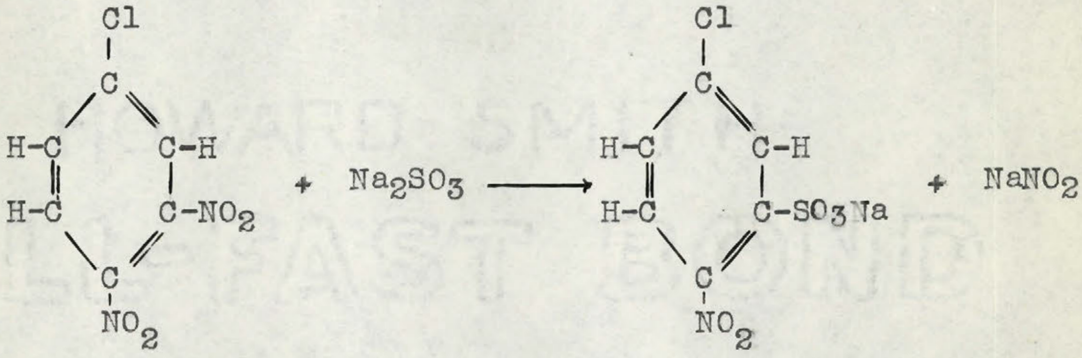


VIII IX

It is a general characteristic of ortho-dinitrobenzene derivatives that one nitro group is labile and through the action of various reagents may be replaced by other groups. Laubenheimer (10) using 1-chloro,-3,4-dinitrobenzene as an ortho-dinitrobenzene derivative showed that the following reaction took place.

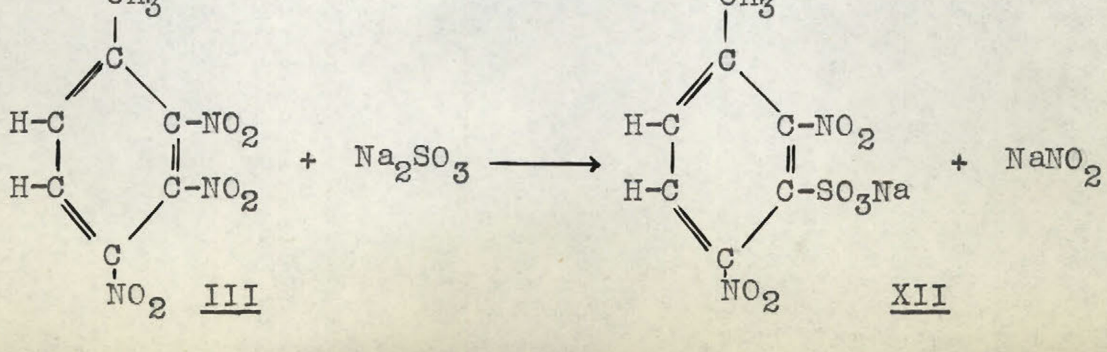


X XI

At the beginning of 1916 (11) this reaction was applied to those unsymmetrical trinitrotoluenes which possess a labile nitro group. It is reported in the literature that the 2,3,4-trinitrotoluene (12), (13), (14), gives 3-methyl, 2,6-dinitroaniline with ammonia and the diphenylamine derivative with aniline, while the 3,4,6-trinitrotoluene gives, with ammonia and aniline, the corresponding compound.

According to Davis (15) it was while looking for a means of rendering the unsymmetrical trinitrotoluenes water-soluble that the sodium sulphite reaction with unsymmetrical trinitrotoluenes was found. It was first attempted to reduce the meta nitro group with sodium polysulphide. Good results were obtained but the purified product contained finely divided sulphur and so the procedure was unsuitable.

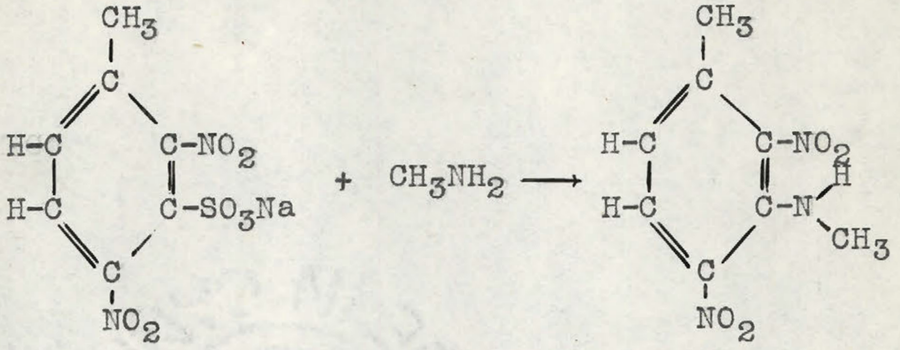
Looking for a more stable reducing agent, sodium sulphite was proposed. Even if it did not react as a reductor, it suited the purpose so well that it was soon generally used. The origin of the commercial procedure is illdefined. In France, it was first believed to be an American procedure whilst concurrently in the United States the process was supposed to be French. We know that the process was in use in France in 1916 (11) and in the United States in 1917 (15). Anyway, the action of sodium sulphite on unsymmetrical trinitrotoluenes was investigated at the beginning of 1916 by the Research Department (11). They investigated the residual liquor of the sodium sulphite purification of trinitrotoluene. The main products of the reaction between the unsymmetrical trinitrotoluenes and sodium sulphite were isolated only in 1924 by Muraour (17) as sodium dinitrotolylsulphonates (XII), but some of their reactions had been known for many years.



III

XII

The Research Department found that those sulphonates behave with methylamine just as the unsymmetrical do with alcoholic $NH_3$, giving substituted dinitrotoluidines.



XII XIII

There is little reported in the literature on the composition of the residual liquor of the sodium sulphite treatment. There may be some work published in Research Department reports 30 et seq. not available to the writer.

The Research Department (11) as well as Brady and Gibson (18) reported that the unsymmetrical trinitrotoluenes can give the following dinitro-3-methyltoluidines upon reaction of their sulphonates with methylamine:

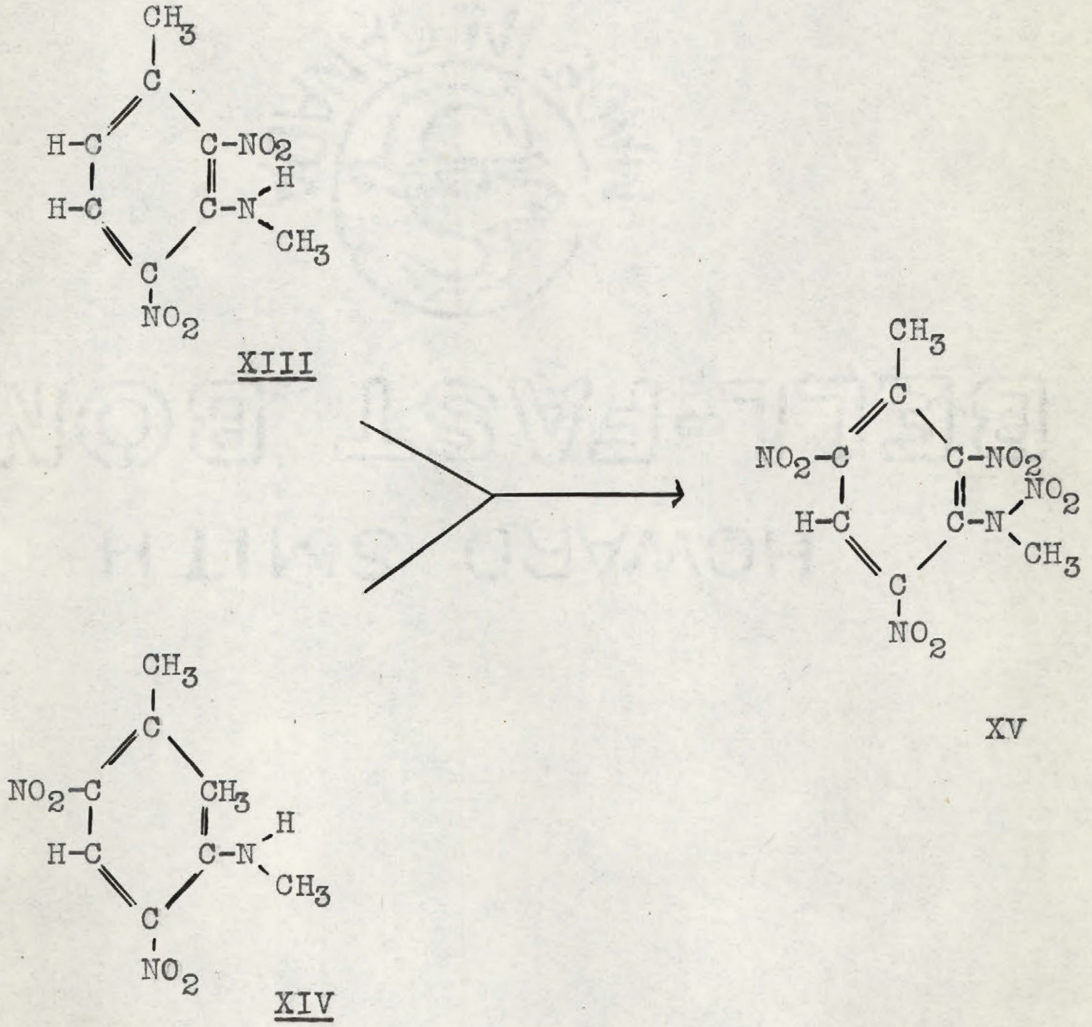
2,4-dinitro-3-methyltoluidine from 2,3,4-trinitrotoluene

4,6-dinitro-3-methyltoluidine from 3,4,6-trinitrotoluene.

The other three unsymmetrical trinitrotoluenes would give the corresponding toluidines were they present in appreciable amount, but, as stated by de Beule (19), the

(IX), (V) and (VII) trinitrotoluenes do not represent 1% of the total product.

From the 2,4- and 4,6-dinitro-3-methyltoluidines (XIII) and (XIV) the Research Department found it possible to obtain a useful explosive. By nitration, the 2,4,6-trinitrotolyl-3-methylnitramine (XV) (11), (18), the methyl homologue of tetryl, was obtained.

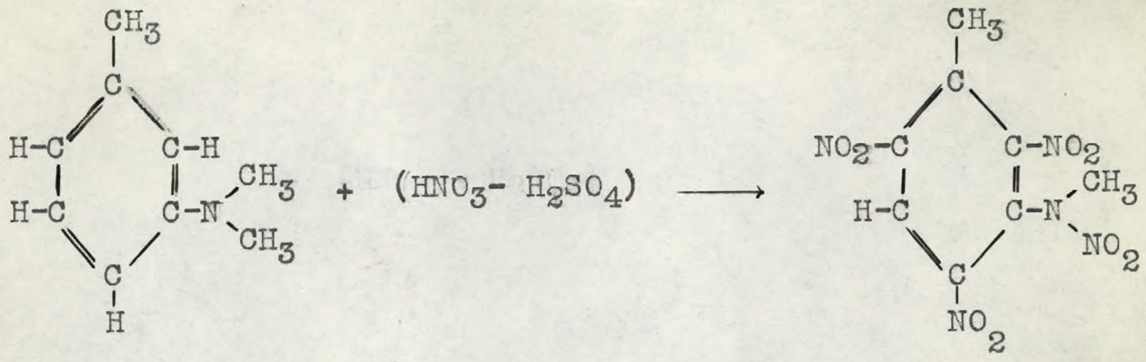


XIII

XIV

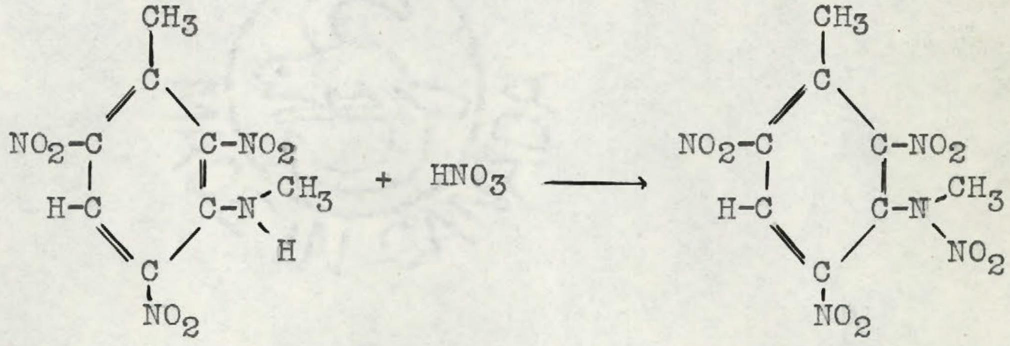
XV

The m-methyltetryl (XV) was first synthesized by Peter van Romburg (20) in 1884, by nitration of the N-dimethyl-m-toluidine (XVI) in mixed acids.



XVI XV

The nitramine was also reported by Blanksma (21) who synthesized it by nitration of the 2,4,6-trinitro-3-N-methyltoluidine (XVII) with fuming nitric acid (d. 1.52).



XVII XV

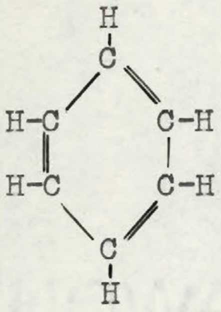
# THEORETICAL DISCUSSION

It is not within the scope of this paper to discuss in detail the structure and properties of the benzene ring, but it seems necessary for the writer to outline in a short summary the theories concerning the electronic concept of the benzene ring and its substitution.

## A. Benzene - Its structure.

The six-membered ring with alternating double bonds as conceived by Kekule, symbolizes the molecule of benzene, but the picture of its accepted structure cannot be represented without making use of the concept of quantum mechanical theory: Resonance.

The idea of resonance, in its application to chemistry, is the following. If it is possible to write for a molecule two or more electronic structures corresponding to about the same energy content and satisfying certain other conditions, then, no one of the structures alone can represent the normal state of the molecule, which, instead is represented essentially by an average of all of them, thus giving to the molecule a lower energy content and by the way rendering it more stable than it would be if it had any one of the structures alone. Such a molecule is a resonance hybrid. According to this theory, benzene resonates between five equivalent structures: the two Kekule isomers, (XVIII) and (XIX), and the three Dewar isomers, (XX), (XXI), (XXII), which are present in very small proportion.



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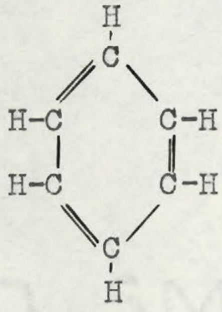

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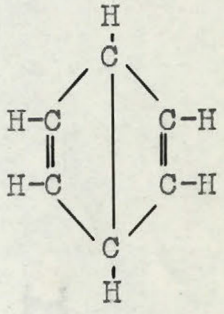

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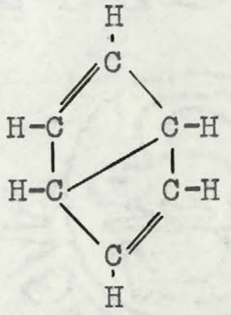

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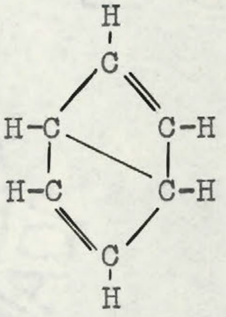
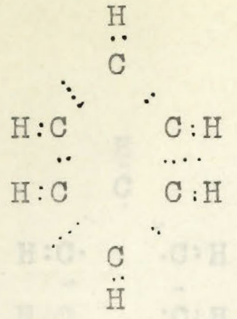


XXII

The electronic structure of benzene as now accepted represents any of the five structures mentioned above. Three important suggestions were made. The Thomson formula (22) (XXIII) is in accord with the three-fold symmetry suggested by the substitution reactions of the benzene nucleus while the centric-formulae of Robinson (23) (XXIV) and (XXV) tend to explain the lack of unsaturation of the benzene ring.



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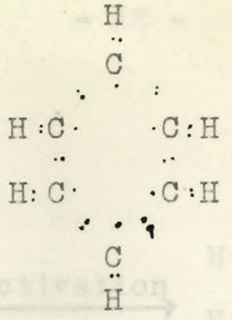

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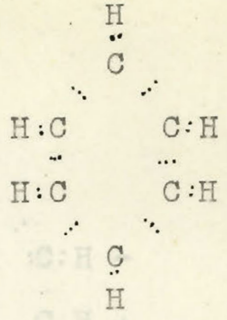
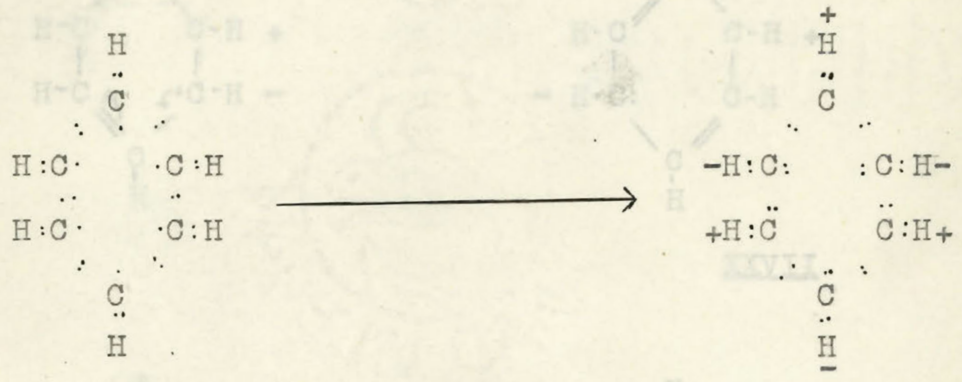


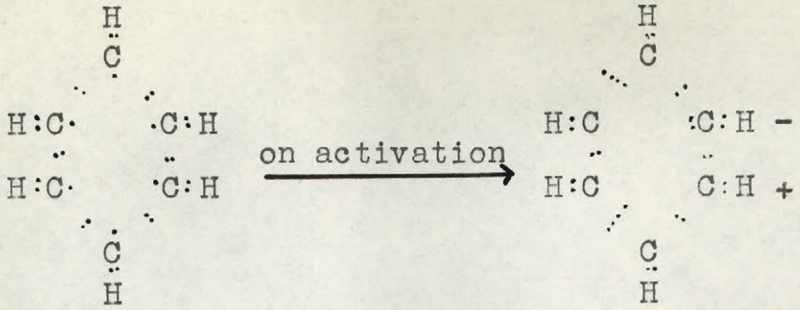
XXV

However, any of these formulae under the influence of an incoming substituent assume the same activated structure. According to Lowry (24) (XXVI), the whole molecule is activated



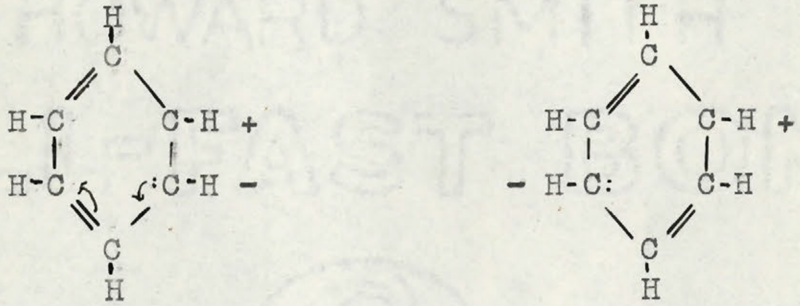
XXVI

while Lapworth and Robinson (23) (25) (26), (XXVII), supposed that a polar activation occurs at a double bond which yields a simple dipole, with two charges only, each of which however is proved to undergo electromeric migration to an alternate position (27), (XXVII) and (XXIX).



XXVII

or



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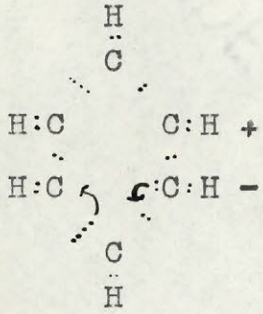

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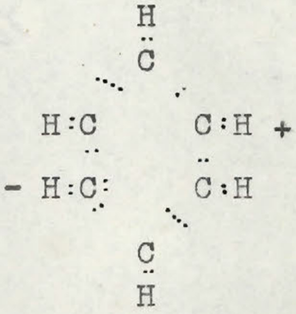


XXIX

B. Orientation in the Benzene Ring.

During the last twenty years a qualitative theory of aromatic substitution has been developed (28); recently a quantitative treatment, based on quantum mechanics (29), has been carried out, with a degree of success which provides strong support for the theory. This theory is based on the consideration of the distribution of electric charges in the molecule in which substitution is taking place. In a benzene ring, the six carbon atoms are equivalent, and the charge distribution is accordingly such as not to make one carbon atom different from another. When a substituent is present, the electron distribution is generally affected in such a way as to change the electron distribution on ortho, meta or para carbon atoms.

Substituents in general can be classified as electron-attracting or electron-releasing groups. They polarize the benzene ring, producing electronic displacement around the nucleus. Inductive displacements (inductive effects) arise mainly from an unequal extent of sharing of the electron pair of a covalent bond and affect the state of polarization of the link. These displacements represent a relatively permanent condition of the molecule. The substituents produce another type of electronic displacement in which their inductive effect is associated to a resonance effect by which the substituent, having an unshared electron pair, tends to increase its covalency. Ingold (30) called this type of electronic displacement "mesomeric effect". The electron-attracting substituents decrease the electron density of the benzene nucleus by inductive effect as in the case of the trimethylammonium ion $+N(CH_3)_3$. A nitro group $NO_2$ (28) represents the type of electron-attracting substituents acting by mesomeric effect. All the electron-attracting substituents are meta orientating and decrease the reactivity of the aromatic nucleus. The electron-releasing substituents increase the electron density of the ring like the alkyl groups, by inductive effect, or like the amino group, by mesomeric effect. By increasing the electron density of the benzene ring, this group of substituents is ortho para directing and facilitates further substitution of the ring.

## I. Aromatic nitration

### (a) Nitration in mixed acids.

It is now believed that nitration of aromatic compounds may take place by an ionic or a free-radical mechanism, (31) the former mechanism being responsible for the nitration with mixed acids. The ionic mechanism of nitration was put forward by Robinson (32) and Ingold (28). As in other substitutions, they considered this reaction as an electrophilic substitution.

It was once generally accepted that, in mixed acids, the sulphuric acid served only as a dehydrating agent which made available a larger quantity of free nitric acid by removing the water present, or that it was reacting with nitric acid (XXX) to form nitric anhydride (XXXII) (33)

$$2\ HNO_3 + H_2SO_4 \longrightarrow N_2O_5 + H_2SO_4\ (aq.)$$

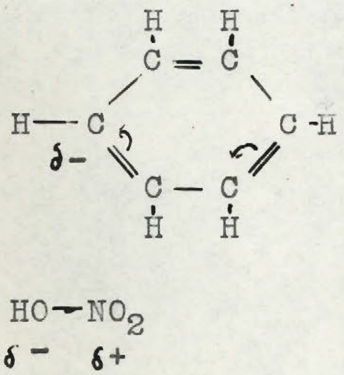
$$\underline{XXX} \quad \underline{XXXI} \quad \underline{XXXII}$$

in which the active nitrating agent would be (34)

$$N_2O_5 \longrightarrow NO_2^+ + ONO_2^- \quad .$$

$$\underline{XXXIII} \quad \underline{XXXIV}$$

Such a mechanism for nitration is unlikely since it was impossible, by spectrographic study of mixtures of sulphuric and nitric acids to detect traces of nitric anhydride (35). Although it is evident that sulphuric acid is a very important reagent in nitration reactions, its function is not seen under the same light by all. Ingold, (28) in his early work, suggested that undissociated nitric acid is responsible for nitration. He assumed a polarization of the molecule (XXXVI) and ionization at the moment of the reaction only (XXXVII).



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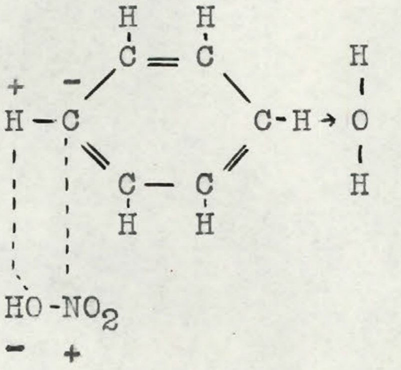
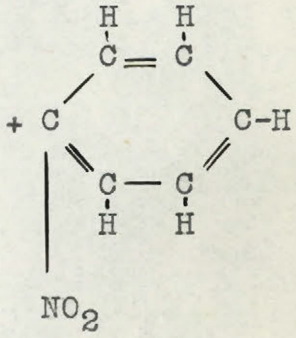


XXXVI



XXXVII

The function of sulphuric acid, according to such an hypothesis, would be to remove the water present in the reaction mixture by forming hydroxonium (XXXVIII) and bisulphate ions.

$$H_2O + H_2SO_4 \longrightarrow \underset{\text{XXXVIII}}{H_3O^+} + HSO_4^-$$

It thus prevents the ionization of nitric acid which is a weaker base than water and, in presence of a strong acid as sulphuric acid, cannot ionize to give hydroxonium (XXXVIII) and nitrate (XXXIX) ions.

$$H_2O + HNO_3 \longrightarrow \underset{\text{XXXVIII}}{H_3O^+} + \underset{\text{XXXIX}}{NO_3^-}$$

Hetherington and Masson (36) in an extremely valuable study of the nitration of nitrobenzene, postulate that undissociated nitric acid is responsible for nitration. They base their postulation on the fact that when a small amount of nitric acid is used, the reaction stops when, in the reaction medium, the number of moles of water is equal to the number of moles of sulphuric acid,

$$H_2O + H_2SO_4 \longrightarrow H_3O^+ + HSO_4^-$$

so that the role of sulphuric acid would be to form hydroxonium ions (XXXVIII) with all water available and ionized nitric acid to give

$$H_3O^+ + NO_3^- + H_2SO_4 \longrightarrow H_3O^+ + HSO_4^- + HNO_3$$

But, as reported by Hantzsch, (35) the nitration of nitrobenzene, with nitric acid alone, stops when the molal concentration of water in the nitration mixture reaches approximately 20%. At this concentration, there is still some undissociated nitric acid. It seems that undissociated nitric acid, cannot, alone, nitrate the aromatic nucleus as postulated by Hetherington and Masson.

In studying the structure of nitric acid Hantzsch (35) concluded that it exists in two forms, the true nitric acid $(NO_3)H$ and a pseudo form in which there is an ester link $NO_2.OH$. On dilution the pseudo nitric acid is transformed to the true nitric acid structure and ionization, increasing with dilution, takes place. With increasing concentration Hantzsch reports that the pseudo acid is converted into nitronium nitrate (XL)

$$3\ HONO_2 \longrightarrow \underline{N(OH)_3^{++}}_{\text{XL}} + 2\ NO_3^- \quad .$$

Hammett (31) gives a modern interpretation to Hantzsch's results. He considers nitric acid as an amphoteric substance which gives in alkaline medium such as water, hydroxonium (XXXVIII) and nitrate ions:

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

In acid media such as sulphuric acid, it behaves as a base and gives nitronium ions (XLI) and bisulphate ions.

$$HNO_3 + H_2SO_4 \longrightarrow (HO)_2N\,O^+ + HSO_4^-$$

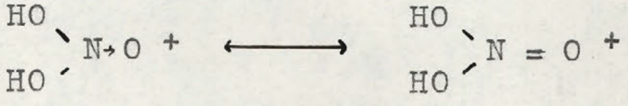
In very strong acid a less reactive nitronium ion is also formed (XL)

$$(HO)_2N\,O^+ + H_2SO_4 \longrightarrow \underset{\underline{XL}}{(HO)_3N^{++}} + HSO_4^-$$

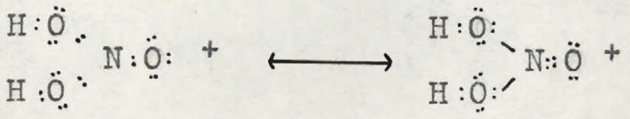
Absolute nitric acid will also dissociate to some extent giving the nitronium ion (XLI).

$$2\,HNO_3 \longrightarrow \underset{\underline{XLI}}{(HO)_2N\,O^+} + NO_3^-$$

The nitronium ion is a resonance hybrid which may well be the nitrating agent (37) in mixed acid as well as in nitric acid alone.

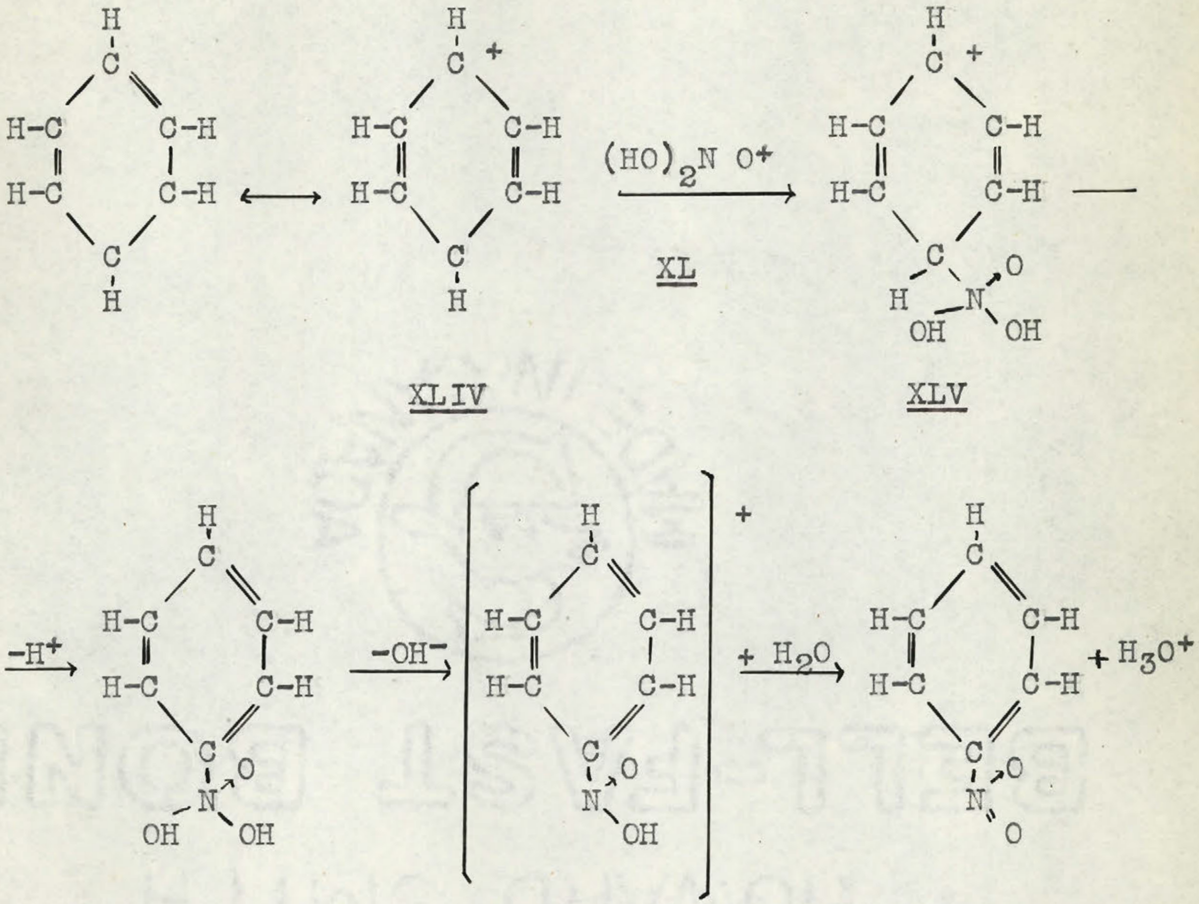


**XL** **XLII**



**XLIII**

A plausible mechanism of nitration in the benzene ring can be outlined as follows (38)



XL

XLIV

XLV

XLVI

The active molecule (XLIV) adds the ion (XL) giving a positive ion (XLV) which, by subsequent loss of a proton and of an hydroxyl group, gives the ion (XLVI). The water formed during the reaction or added to dilute the reaction mixture at the end of the reaction, deactivates ion (XLVI) to nitrobenzene. Hetherington and Masson (36), (39) consider the ion (XLVI) as the ionic form of nitrobenzene which is nitrated to the dinitro derivative.

The function of sulphuric acid in nitrating mixtures seems, as inferred from the previously mentioned hypothesis, to be a source of ions. It prevents the ionization of nitric acid by formation of nitronium and bisulphate ions:

$$HNO_3 + H_2SO_4 \longrightarrow (HO)_2N\,O^+ + HSO_4^-$$

and reacts with water to give hydroxonium and bisulphate ions,

$$H_2O + H_2SO_4 \longrightarrow H_3O^+ + HSO_4^-$$

so that the nitronium ions, which are believed to be the nitrating agent, are not destroyed by water to give hydroxonium and nitrate ions.

$$H_2O + (HO)_2N\,O^+ \longrightarrow H_3O^+ + NO_3^-$$

(b) Nitration in neutral solvent.

As previously stated, Hantzsch (35) in his study on nitric acid mentioned that concentrated nitric acid is dissociated to some extent into nitronium and nitrate ions. He also reported that in the nitration of nitro-benzene with nitric acid alone, the reaction stops when the concentration of water present reaches about 20%. We assume that the reaction, in fuming nitric acid proceeds through an ionic mechanism as in mixed acids, where sulphuric acid is acting as solvent and as ionizing agent. Then, we are in the presence of two equilibrium reactions, whose rates are markedly different. The reaction products of the fast reaction inhibit the slower one.

If we consider the dissociation of nitric acid into nitronium and nitrate ions:

$$2\ HNO_3 \rightleftharpoons (HO)_2NO^+ + NO_3^- \qquad (a)$$

it is evident that this reaction is affected by water in two different ways. Water, being a stronger base than nitric acid, will give with nitronium ions, undissociated nitric acid and hydroxonium ions:

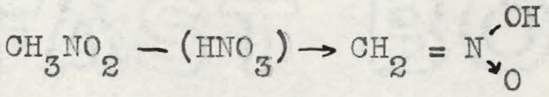
$$(HO)_2N\ O^+ + H_2O \rightleftharpoons H_3O^+ + HNO_3$$

However, on account of its greater concentration, nitric acid will react faster with water than nitronium ions, thereby increasing the concentration of nitrate ions:

$$H_2O + HNO_3 \rightleftharpoons H_3O^+ + NO_3^-$$

which, according to the law of mass action, will shift reaction (a) toward the left, thus inhibiting the formation of nitronium ions. This is mere speculation as no direct evidence is available other than the fact that all aromatic nitrations carried out in nitric acid alone require considerable excess of nitric acid.

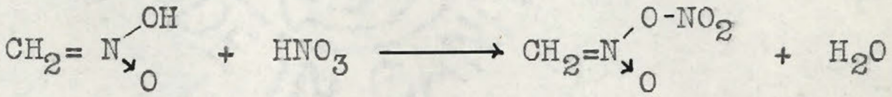
Ingold, (38) in studying nitration in inert solvents such as nitromethane, came to the conclusion that in this case the nitration proceeded through a chain reaction. The fundamental chain mechanism is initiated by isomerization of nitromethane to its aci-form (XLVII) This isomerization is catalyzed by nitric acid:



$$CH_3NO_2 - (HNO_3) \rightarrow CH_2 = N\begin{smallmatrix} \diagup OH \\ \searrow O \end{smallmatrix}$$

XLVII

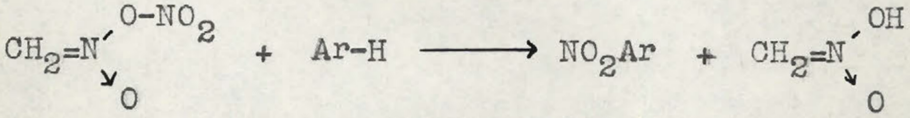
The aci-form (XLVII) reacts with nitric acid to give (XLVIII):



$$CH_2 = N\begin{smallmatrix} \diagup OH \\ \searrow O \end{smallmatrix} + HNO_3 \longrightarrow CH_2 = N\begin{smallmatrix} \diagup O-NO_2 \\ \searrow O \end{smallmatrix} + H_2O$$

XLVIII

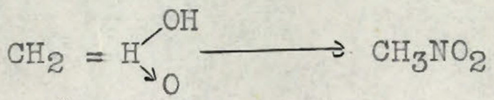
The intermediate (XLVIII) is the effective nitrating agent reacting with the aromatic nucleus to give the aromatic nitro compound (XLIX)



$$CH_2 = N\begin{smallmatrix} \diagup O-NO_2 \\ \searrow O \end{smallmatrix} + Ar-H \longrightarrow NO_2Ar + CH_2 = N\begin{smallmatrix} \diagup OH \\ \searrow O \end{smallmatrix}$$

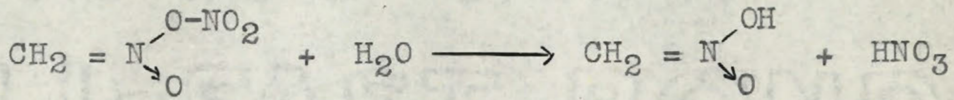
XLIX XLVII

The last equation illustrates the nitration of the aromatic nucleus and the conservation of the chain carrier (XLVII) which may be destroyed by reforming nitromethane.



$$CH_2 = H\begin{matrix}\diagup OH \\ \searrow O\end{matrix} \longrightarrow CH_3NO_2$$

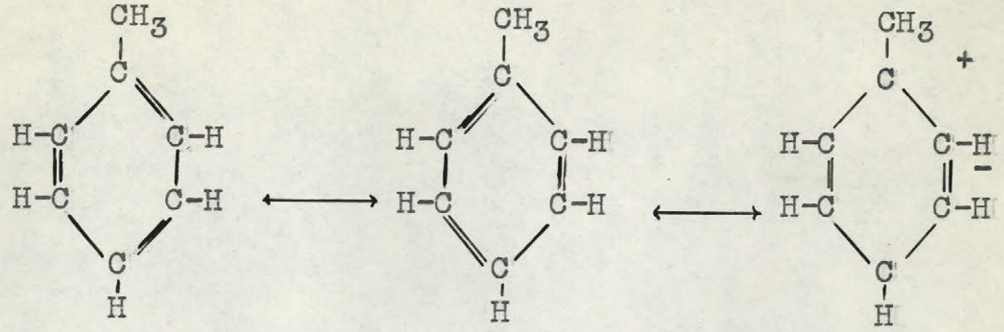
The nitrating agent (XLVIII) is deactivated by water giving the aci-form of nitromethane and nitric acid.

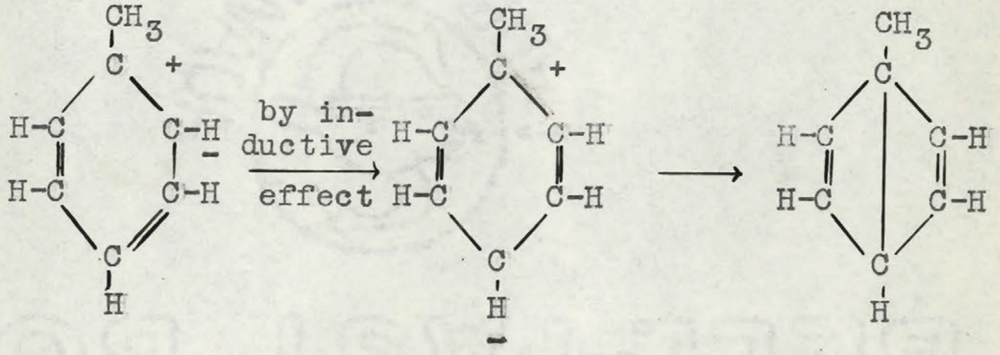


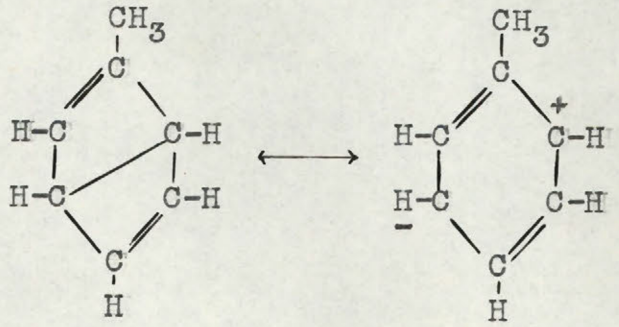
$$CH_2 = N\begin{matrix}\diagup O{-}NO_2 \\ \searrow O\end{matrix} + H_2O \longrightarrow CH_2 = N\begin{matrix}\diagup OH \\ \searrow O\end{matrix} + HNO_3$$

## II. Nitration of Toluene

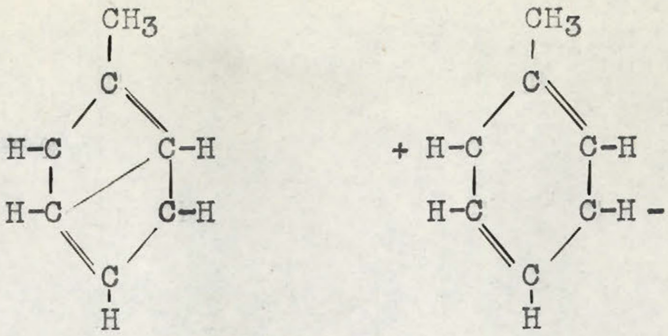
Toluene or methylbenzene possesses an electron-releasing substituent which exerts its orientation by inductive effects. During the nitration of toluene, the Methyl group orients the nitro groups in ortho- and para positions. By considering the different resonating structures of benzene, it is possible to explain the production of meta derivatives as being formed from the excited structures (L), (LI), which contribute in a very small proportion. (24).







L

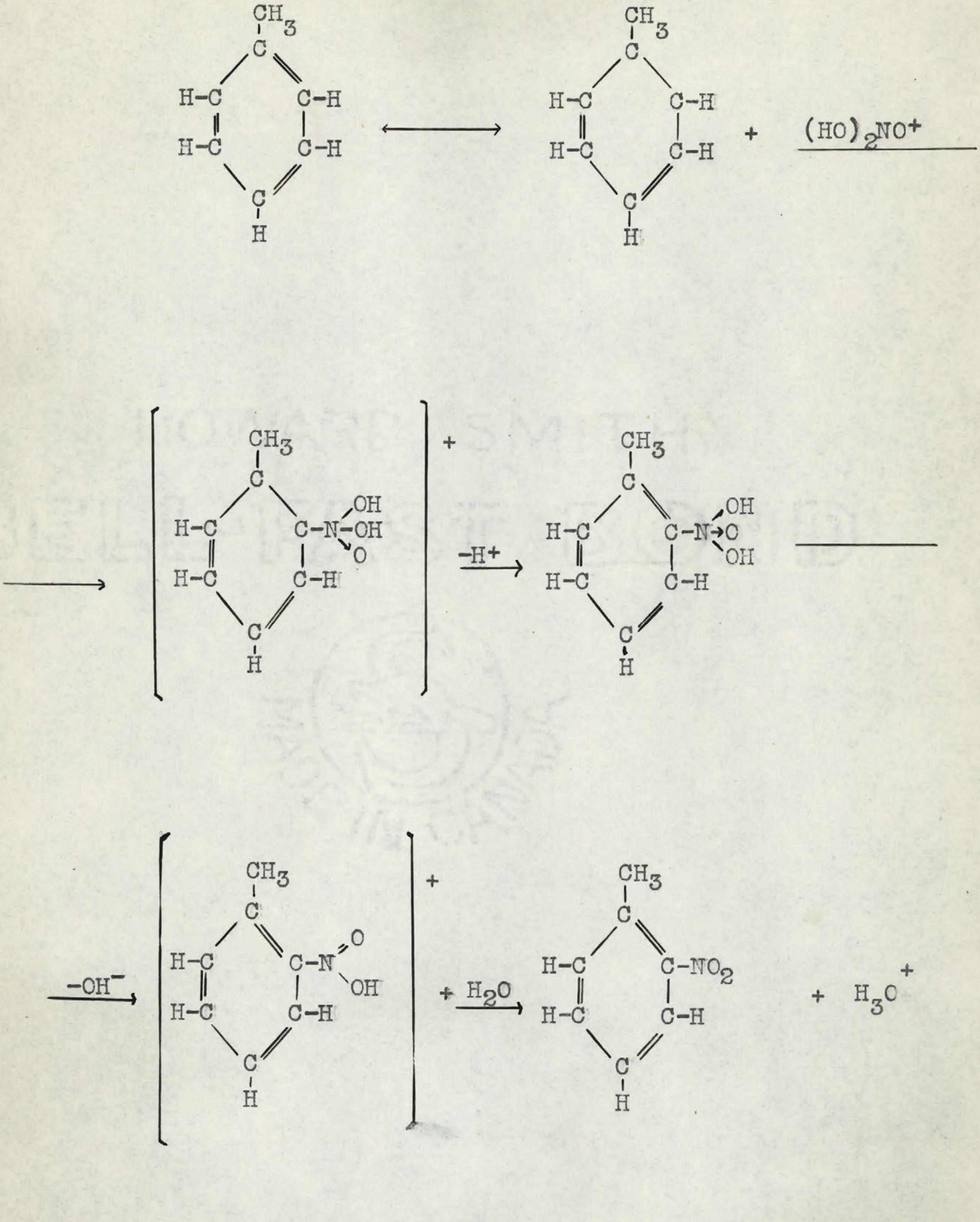


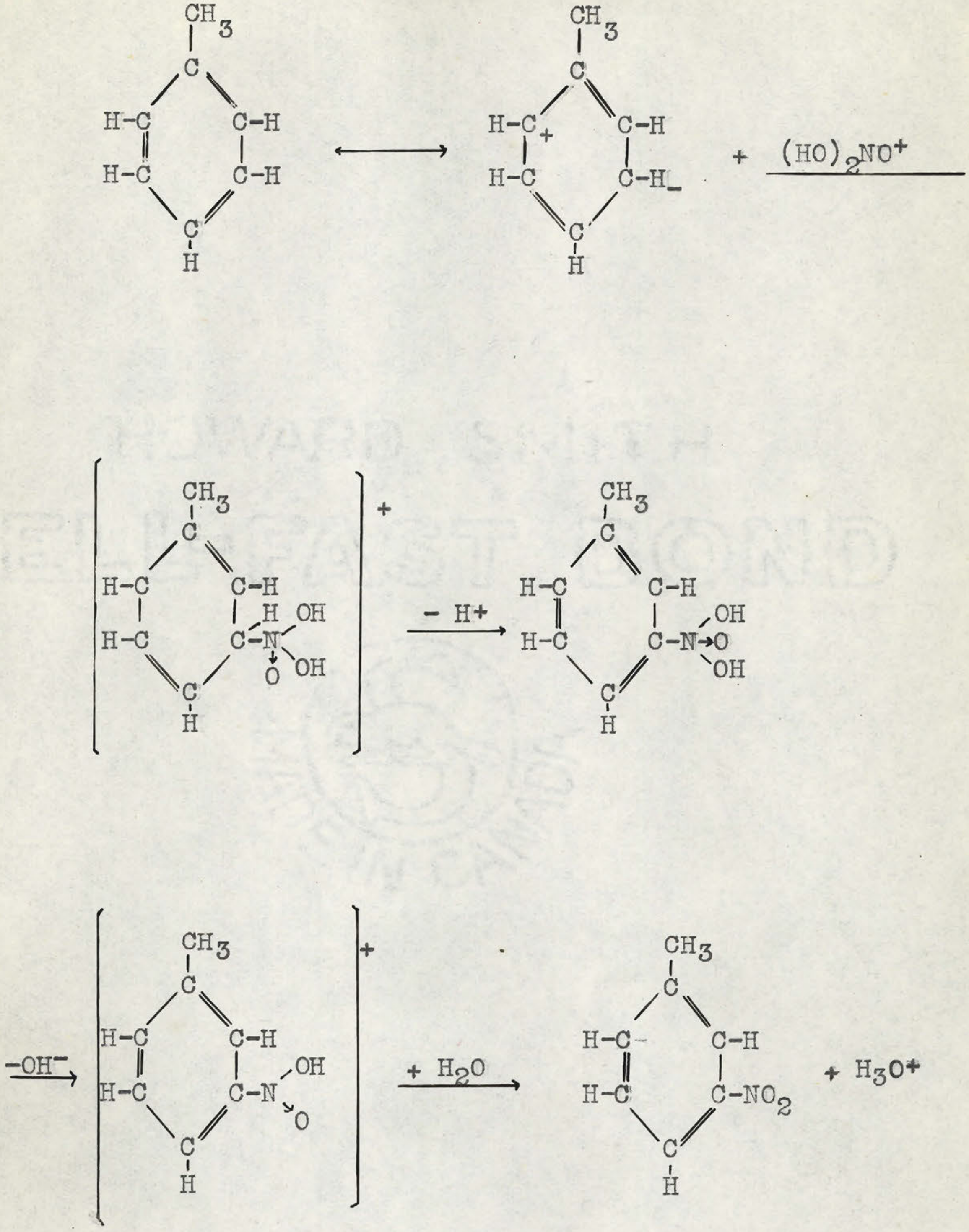
LI

Nitrated by mixed acids, toluene gives (19) on mononitration a mixture formed of

| | |
|---|---|
| ortho-nitrotoluene | 59.2% |
| para-nitrotoluene | 36.1% |
| meta-nitrotoluene | 4.7% . |

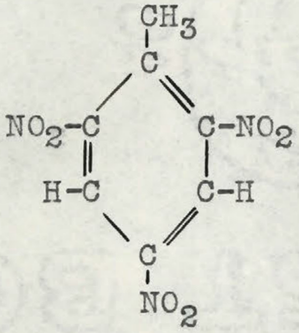
The nitration follows the general mechanism of aromatic nitration and we may assume that the excited structures of the benzene nucleus are responsible for the meta-nitro derivative formed.


(HO)₂NO⁺
-H⁺
-OH⁻
+ H₂O
+ H₃O⁺
-NO₂

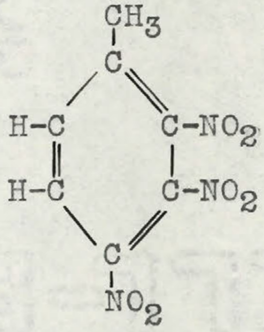

CH3
H-C
C-H
+
C-H_
(HO)2NO+
- H+
H
OH
C-N
O
-OH-
+ H2O
C-NO2
+ H3O+

The same mechanism can be applied for para substitution as well as for the introduction of the other two nitro groups on the nucleus.

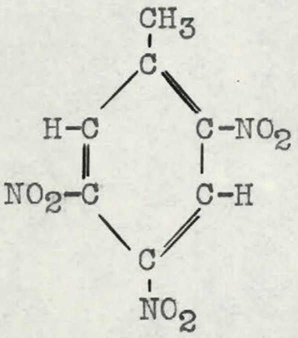
The product of complete nitration of toluene is formed of a mixture of six isomers (LII). The symmetrical isomer forms 95.5% of the mixture.



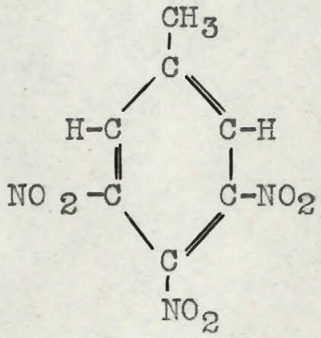
α -TNT 95.5%



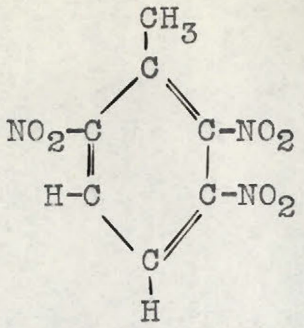
β -TNT 1.49%



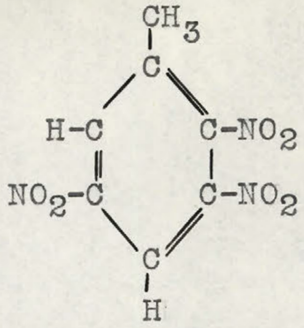
γ -TNT 2.58%



δ -TNT 0.006%



η-TNT 0.34%



ε-TNT 0.032%

## III. Nitration of Substituted Aromatic Amines

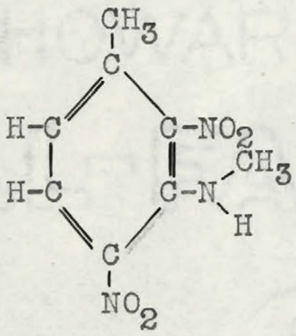
As indicated by Clemo and Smith (40), the nitration of substituted aromatic amines is somewhat more complex than pictured in the preceding section. In their investigation, they reported that para-chloro-NN-dimethyl aniline gives, on nitration, different products when different concentrations of sulphuric acid are used. With 75% sulphuric acid, the ortho-nitro derivative is obtained while the meta-nitro-para-chloro-NN-dimethyl aniline is obtained when concentrated acid (92%) is used. With sulphuric acid of intermediate concentration, mixtures of different composition are obtained.

The meta nitration seems to be explained by the formation of the ammonium salt in concentrated sulphuric acid, but it is impossible to believe that no ammonium ions are present in 75% sulphuric acid. The fact that the meta nitration proceeds with greater ease than ortho nitration seems to indicate that these two isomers are produced through two different mechanisms.

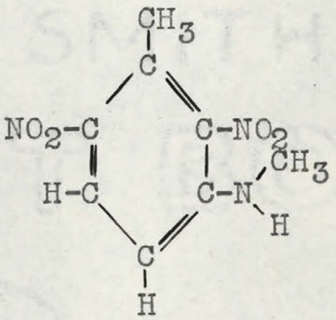
The meta nitration can be explained by considering the influence of the para substituent. The latter diminishes the negativity of the amino group (41) thus favouring the meta substitution. When the nitration is carried out in concentrated sulphuric acid, the meta orientating effect of the dimethylammonium ion is enhanced by the ortho directing effect of the para halogen and accounts for the anomalous ease of meta nitration compared with the ortho substitution.

In studying the inversion of phenylnitramine into nitrophenylamines, Macciotta (41) confirmed the work of Orton and Bradfield (42). While investigating the nitramine rearrangement, these authors found that phenylnitramine in acid medium rearranged to ortho-nitroaniline instead of para- as is often the case with N-substituted anilines. Macciotta (41) found that if there is a substituent in meta position to the amino group, the compound behaves as the mononitroso derivative and gives the para-nitroaniline.

Similarly, the nitration of 2,4- or 2,6-dinitro-3-N-methyltoluidine (XIII), (XIV) to the nitramine (XV) involves a nitramine rearrangement.

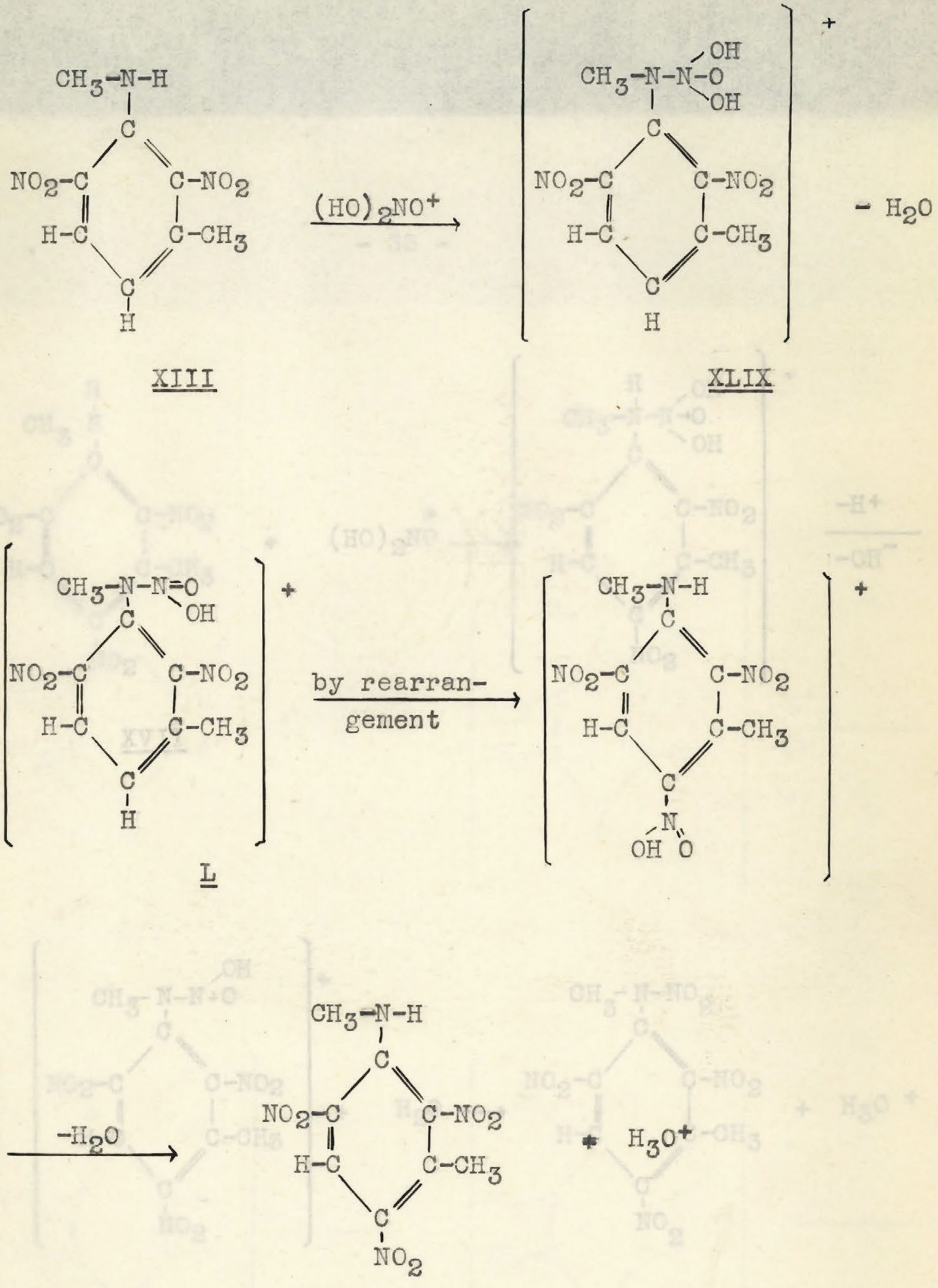


XIII



XIV

The toluidine (XIII) on nitration will give a nitramine (L) which rearranges to the para position to give the 2,4,6-trinitro-3-N-methyltoluidine (XVII) (21), which undergoes nitration to give the final product, m-methyltetryl (XV).

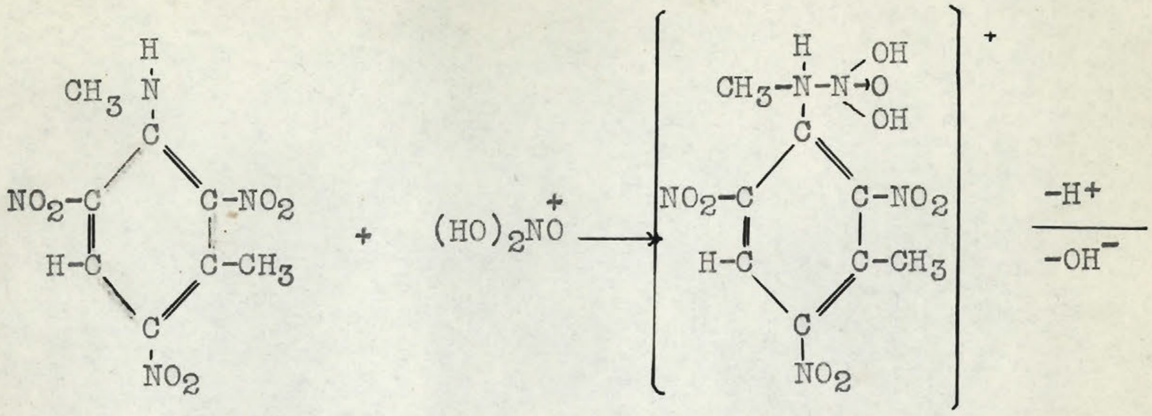


XIII

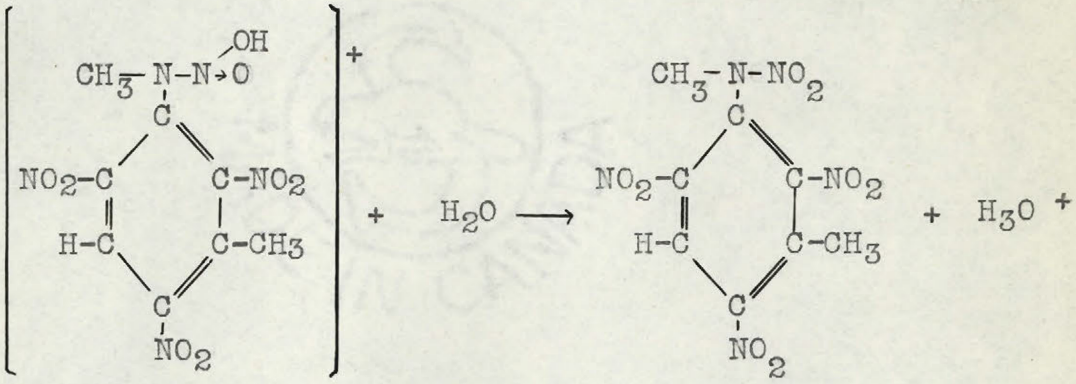
XLIX

L

XVII

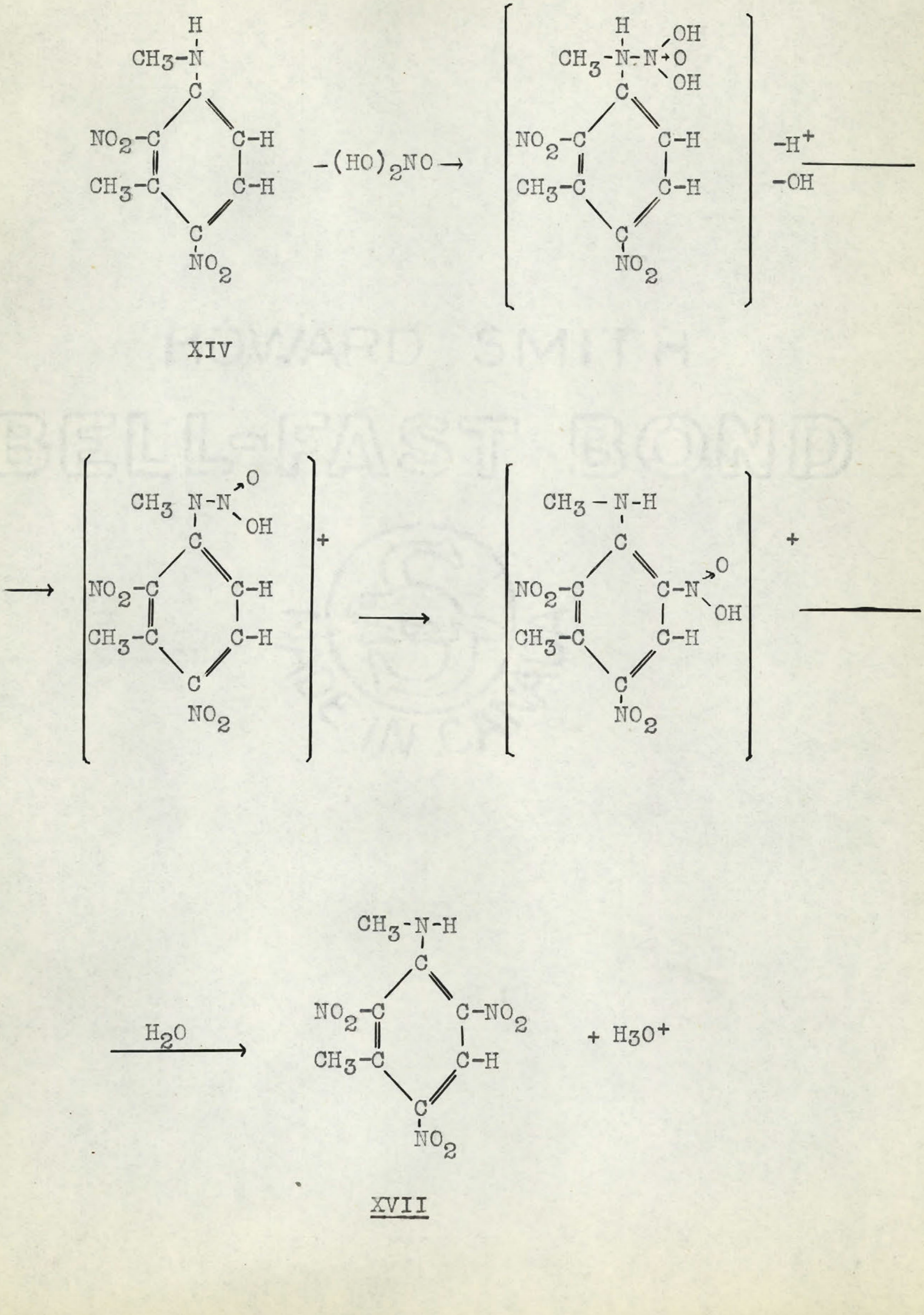


XVII



XV

The 2,6-dinitro,3-N-methyltoluidine (XIV) will give the trinitrotoluidine (XVII) by a slightly different mechanism. Since one of the ortho positions to the amino group (the 4-carbon atom) is unsubstituted, the migration of the nitro group will take place to this carbon.



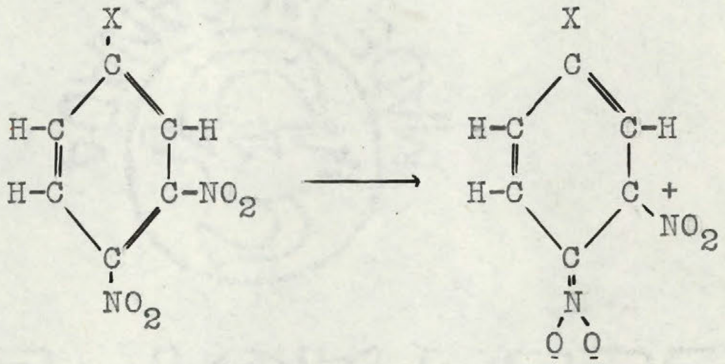
XIV

XVII

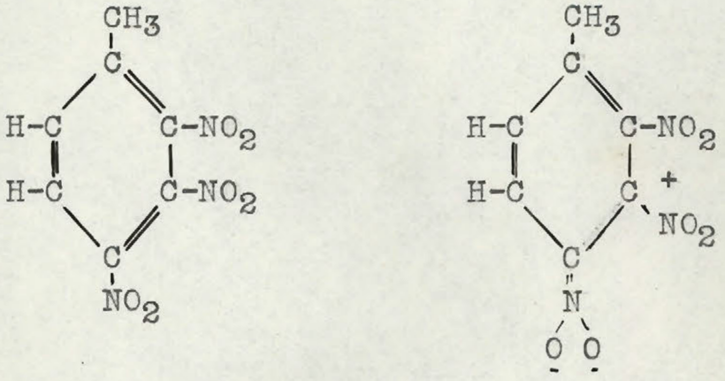
The trinitrotoluidine (XVII) will give the nitramine (XV) by the same mechanism as above described.

## IV. Anomalous Property of Polynitro Substituted Benzene

If we consider the structure of ortho-dinotrobenzene derivatives, it is evident that by mesomeric displacement one of the positions occupied by the nitro group will be activated towards nucleophilic reagents (LIII).

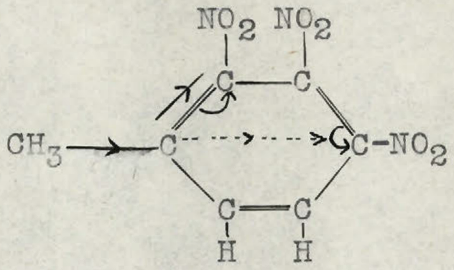


LIII



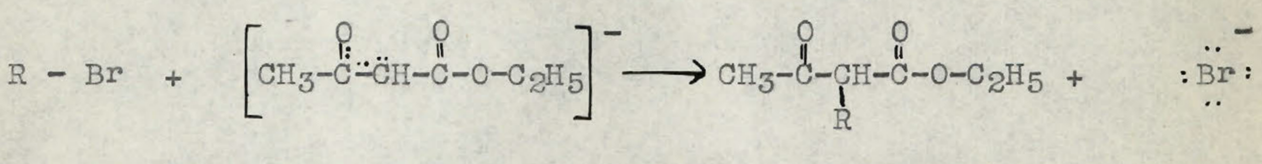
LIV

By such a mechanism the 3 position becomes positively charged and will attract any neighbouring nucleophilic reagent. In trinitro derivatives of toluene inductive effect also takes place; the methyl group orients the



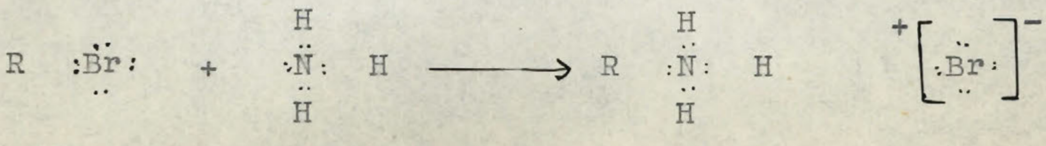
electrons in ortho and para positions at the same time decreasing the electron density of the meta position (43). Both effects are additive and they render the meta position (LIV) the ideal site of a nucleophilic displacement reaction on carbon (31). This important type of reaction involves the direct replacement of one group attached to carbon by another that carries an unshared electron pair. It is nucleophilic because the driving force is the nucleus-seeking tendency of the unshared pair.

A familiar example is the alkylation of sodium acetoacetic ester.



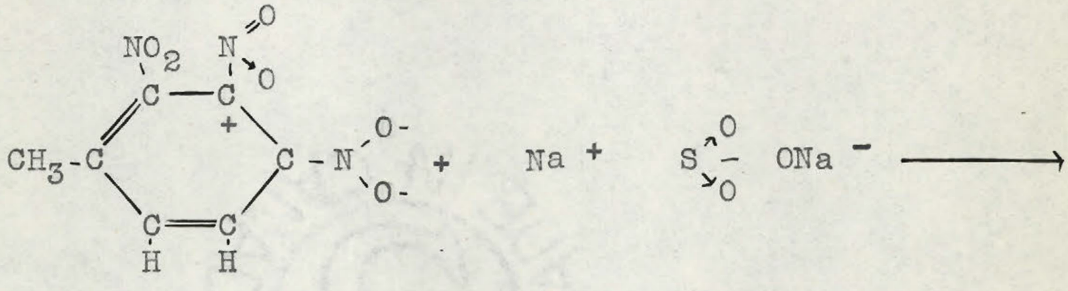
$$R - Br + \left[ CH_3-\overset{O}{\overset{\vdots}{C}}\overset{..}{-}\overset{..}{C}H-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \right]^- \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}-O-C_2H_5 + \;:\overset{..}{\underset{..}{Br}}:^-$$

The same type of reaction can be applied to the alkylation of amines (31).

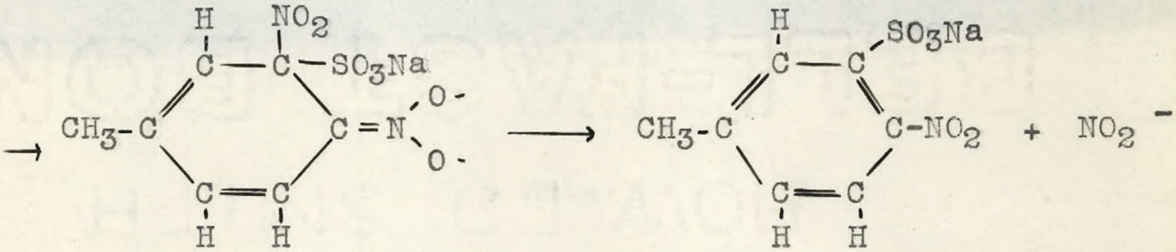


$$R \; :\overset{..}{\underset{..}{Br}}: \; + \; \overset{H}{\underset{H}{:\overset{..}{\underset{..}{N}}:}} \; H \longrightarrow R \; \overset{H}{\underset{H}{:\overset{..}{\underset{..}{N}}:}} \; H \quad {}^{+}\left[ :\overset{..}{\underset{..}{Br}}: \right]^-$$

An analogous mechanism can be applied to the displacement of the meta nitro group of the unsymmetrical trinitrotoluenes by sodium sulphite. The nucleophilic reagent possesses an unshared electron pair and as above, the unsymmetrical trinitrotoluenes become positively charged at the meta carbon atom (LIV).



LIV

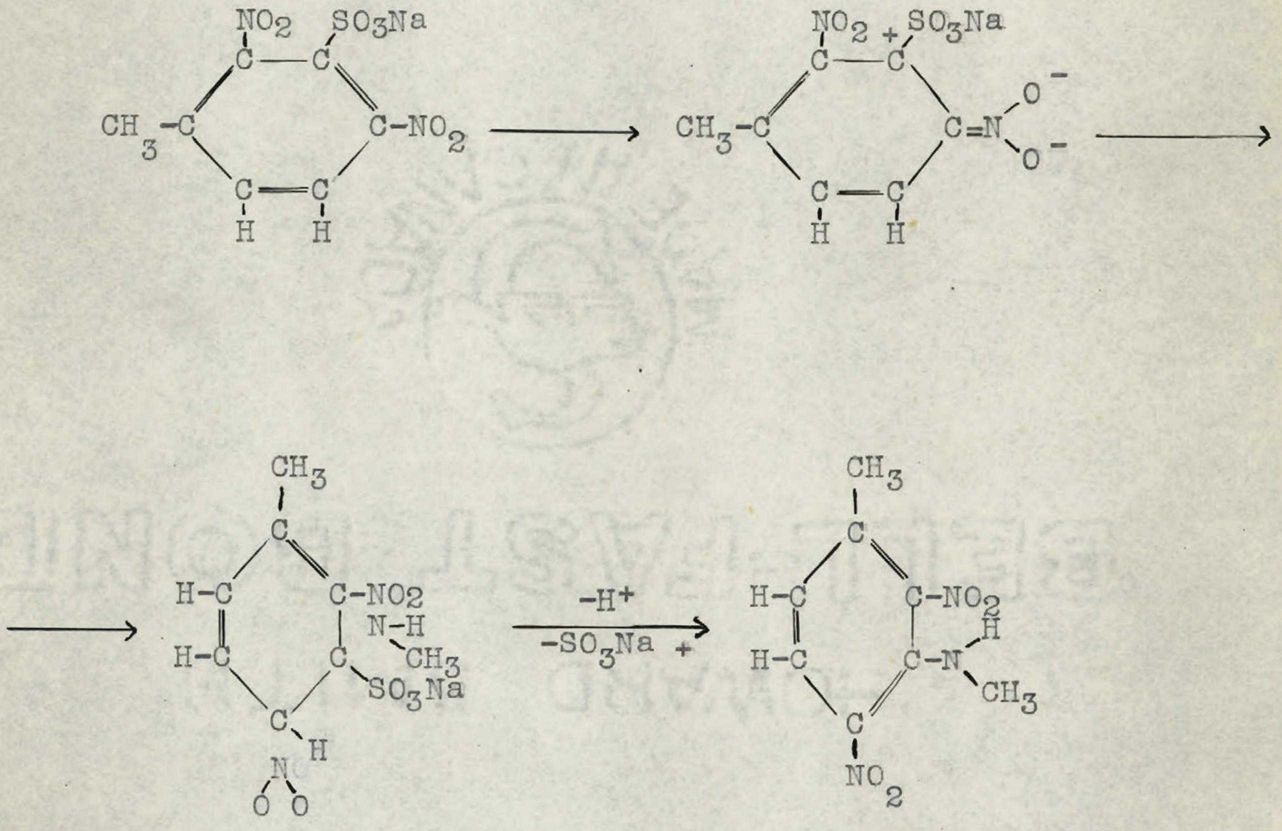


LV

If we consider the sodium sulphonate (LV) thus obtained, it is possible to submit it to an analogous displacement by using a stronger nucleophilic reagent, e.g., methylamine. This nucleophilic reaction is affected by the basicity of the reaction medium. In water, methylamine gives

$$CH_3NH_2 + H_2O \longrightarrow (CH_3NH_3)^+ \quad OH^-$$

In increasing the hydroxyl ion concentration in such a way that the equilibrium being shifted to the left, nucleophilic displacement on carbon is possible, and we have



## CONSIDERATION OF REAGENTS

The purification of crude trinitrotoluene is actually carried out in all the Canadian explosive factories by the so-called sodium sulphite process. This method of purification eliminates the unsymmetrical isomers by transforming them into soluble sodium dinitrotolyl-m-sulphonates. In the modern factories of Defence Industries Limited, a one-step procedure is in use and can be described as follows.

The crude hot trinitrotoluene comes out of the nitrator as an oil which is first washed with hot water until free from acid. The temperature of molten trinitrotoluene is rapidly decreased by the addition of a certain amount of cold water. It then forms a slurry to which a diluted solution of sodium sulphite is added in such a quantity that the ratio of solid trinitrotoluene to solid sodium sulphite is 1: 0.091. Crystallization starts very rapidly and very fine crystals are formed. It is assumed that the impurities contained in the oily mass of hot trinitrotoluene are occluded on the surface of the solid particles (16). The material to be purified is continually stirred during the above operations. At the end of the sodium sulphite wash, the magma is pumped through a filtering device. The filtrate is the so-called Sellite wash liquor. The purified trinitrotoluene is then washed with cold water until free from Sellite liquor, and dried.

As all the water used in this last wash goes through the same drainage system as the Sellite liquor itself, a very dilute solution of sodium dinitrotolyl-m-sulphonates is obtained. However, if the industrial preparation of m-methyltetryl (XV) from the dinitro-3-N-methyltoluidines obtained from the Sellite wash liquors were undertaken, it would be possible to devise a system whereby the Sellite liquor would be diverted from the wash liquor and obtained undiluted.

For the purification of trinitrotoluene, Canadian Industries Limited at McMasterville, Que., use the sodium sulphite method but their procedure is quite different from that previously described. Carried out at a temperature of ± 90° C., it can be described as follows.

The crude hot trinitrotoluene is given two hot washes with water to free it from acid; then it is submitted to a first wash with a sodium sulphite solution. This gives the first Sellite wash. When the first liquor has been drained off, the molten trinitrotoluene is again treated with a sodium sulphite liquor containing boric acid which buffers the solution to maintain pH 7 - 8.3 (46). This forms the second Sellite wash liquor. After the second sodium sulphite purification, the hot trinitrotoluene is washed twice with hot water and then crystallized. The Sellite liquors thus obtained contain an appreciable amount of dissolved trinitrotoluene and are saturated with sulphur dioxide. Before amination, these two substances must be removed. These waste liquors are not diluted by the wash water like those obtained with the procedure first mentioned.

The amination of the sodium dinitrotolyl-3-sulphonates was carried out with the purest methylamine commercially available. An aqueous solution of methylamine (33%) was used for the earlier part of the work. As this solution contained an appreciable amount of ammonium hydroxide, it was decided to use the methylamine hydrochloride which is not completely free from ammonium chloride, but is the purest material available.

For industrial uses, methylamine would have to be imported from the United States as it is not being prepared in Canada. In order to arrive at a production cost of m-methyltetryl, Mr. K. Cheetham of the Department of Munitions and Supply, inquired at the United States Army Ordnance and was given a U.S. market price for pure methylamine of $0.63/lb. However, the manufacturers quote a special price of $0.40/lb. for the American Ordnance; this price would presumably apply to Canadian war orders. However, it would undoubtedly be possible to prepare methylamine at a cheaper price. If we consider the procedure now in use, methylamine is synthesized by passing methanol vapors and gaseous ammonia over thorium oxide. The reaction product is a mixture of mono-, di-, and trimethylamine. By fractional distillation, it is possible to obtain a separation of this complex mixture.

The nitration of the dinitro-3-N-methyltoluidines is carried out in concentrated nitric acid and in mixed acids. These are readily available at any explosive plant. The concentrated nitric acid (95 - 96%), including the cost of recovery, is quoted at $0.03/lb. ± 0.005, while the concentrated sulphuric acid costs $0.006 per pound. Another acid used for nitration is the so-called "antifreeze-mixture" formed of 84.5% of nitric acid, 12.2% of sulphuric acid and 3.3% of water. This mixture, having a very low freezing point, is very handy as it can be shipped in ordinary tank cars or used in cast iron reactors without doing any damages by corrosion.

# EXPERIMENTAL

## A. Amination

The amination of the sodium dinitrotolyl-m-sulphonates of the Sellite wash liquors was known to be possible (11), (16). As there was no procedure established, it was attempted, by the writer, to find the optimum conditions for preparing the dinitro-3-N-methyltoluidines from those liquors. Three variables had to be determined: temperature, duration of reaction and the optimum concentration of methylamine.

### 1. Optimum concentration of methylamine.

To start, two variables had to be arbitrarily fixed. Considering the reagents, it was decided that the reaction time would be two hours and the temperature of reaction 45 - 50° C. Then, the determination of the optimum concentration of methylamine to be used was undertaken. The following procedure was used.

> 50-ml. samples of slightly alkaline Sellite wash liquors were treated with increasing amounts of methylamine. The reaction was carried out in an open flask. The solution was stirred at 45 - 50°C. for two hours. The resulting mixtures, after cooling to room temperature, were placed in an ice-box for 15 hours. After this period of

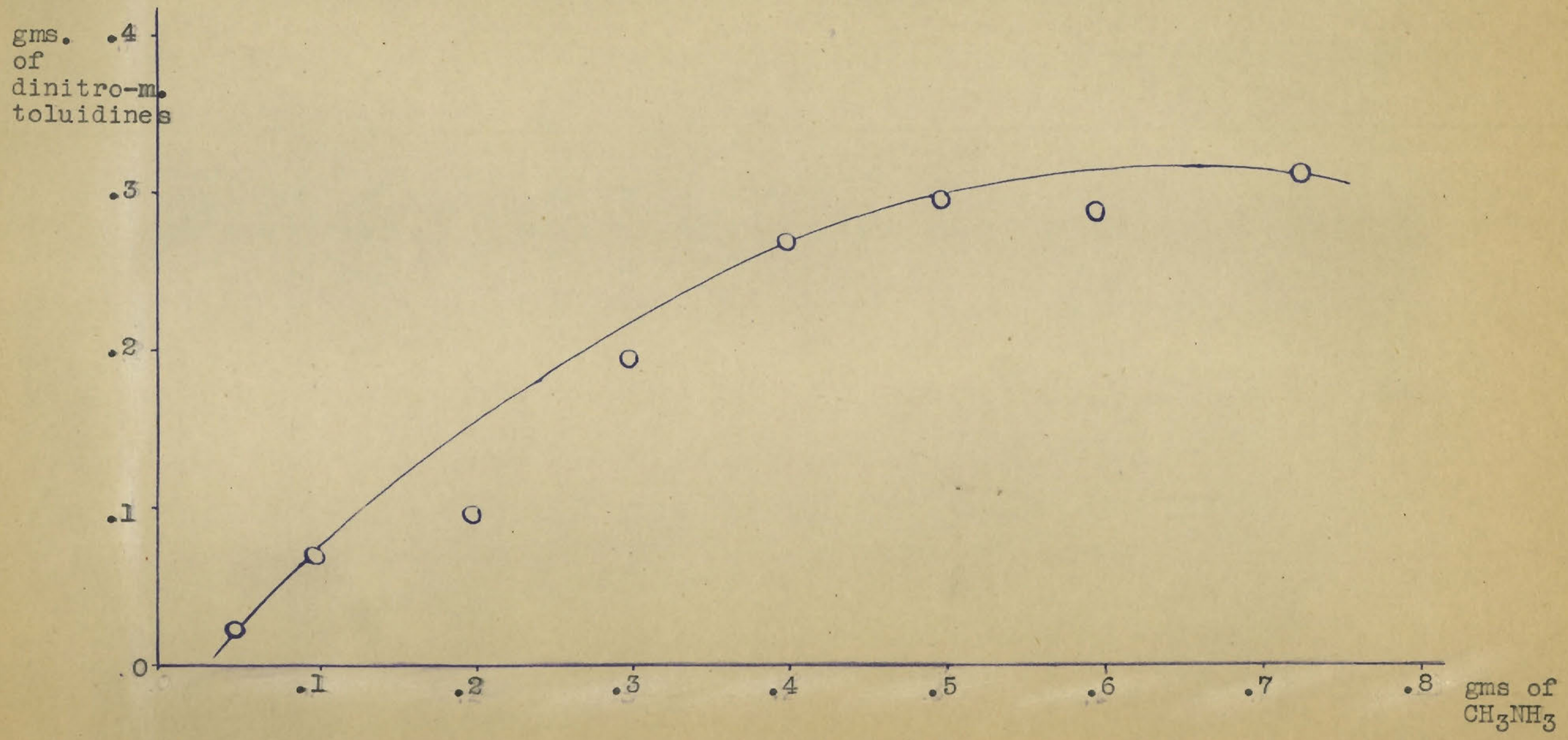
standing, the precipitate was filtered off on a tared Gooch crucible, rapidly washed with cold distilled water and dried by an air current or in a vacuum desiccator to constant weight.

The following results were obtained.

TABLE I

| Run No. | Volume of liquor in ml. | $CH_3NH_2$ in gms. | Dinitro-3-N-methyl-toluidines in gms | |
|---|---|---|---|---|
| | | | Sellite 1st | Sellite 2nd |
| 1 | 50 | 0.0495 | 0.024 | - |
| 2 | 50 | 0.099 | 0.070 | - |
| 3 | 50 | 0.198 | 0.093 | - |
| 4 | 50 | 0.297 | 0.197 | - |
| 5 | 50 | 0.396 | 0.270 | 0.99 |
| 6 | 50 | 0.495 | 0.297 | 1.213 |
| 7 | 50 | 0.594 | 0.288 | 1.312 |
| 8 | 50 | 0.725 | 0.312 | 1.314 |

From these results it was concluded that under these conditions, 11.88 gms. of methylamine per litre of Sellite wash liquor would be the optimum concentration. However, it was noticed that by evaporation, the concentration of methylamine in the reaction mixture was considerably decreased. Some amination re-



GRAPH I

actions were done using a closed reaction flask equipped with a mercury-sealed stirrer, and a 17.7% increase in yield was noted as shown below.

TABLE II

| Run No. | Reaction flask | $CH_3NH_2$ in gms. | Volume of Sellite 1st in ml. | Dinitro-3-N-Methyl-toluidines in gms. | % Differ- |
|---|---|---|---|---|---|
| 9 | open | 0.297 | 50 | 0.197 | 17.7% |
| 10 | closed | 0.297 | 50 | 0.232 | |

When the reaction is carried out in a closed system, it proceeds under a slight pressure of approximately 5/8" of mercury.

At the beginning of the preceding group of runs it was noticed that the reaction took place only if the solution was slightly alkaline. This slight alkalinity decreases the amount of methylammonium ions, but a great

$$CH_3NH_2 + H_2O \longrightarrow [CH_3NH_3]^+ \quad [OH]^-$$

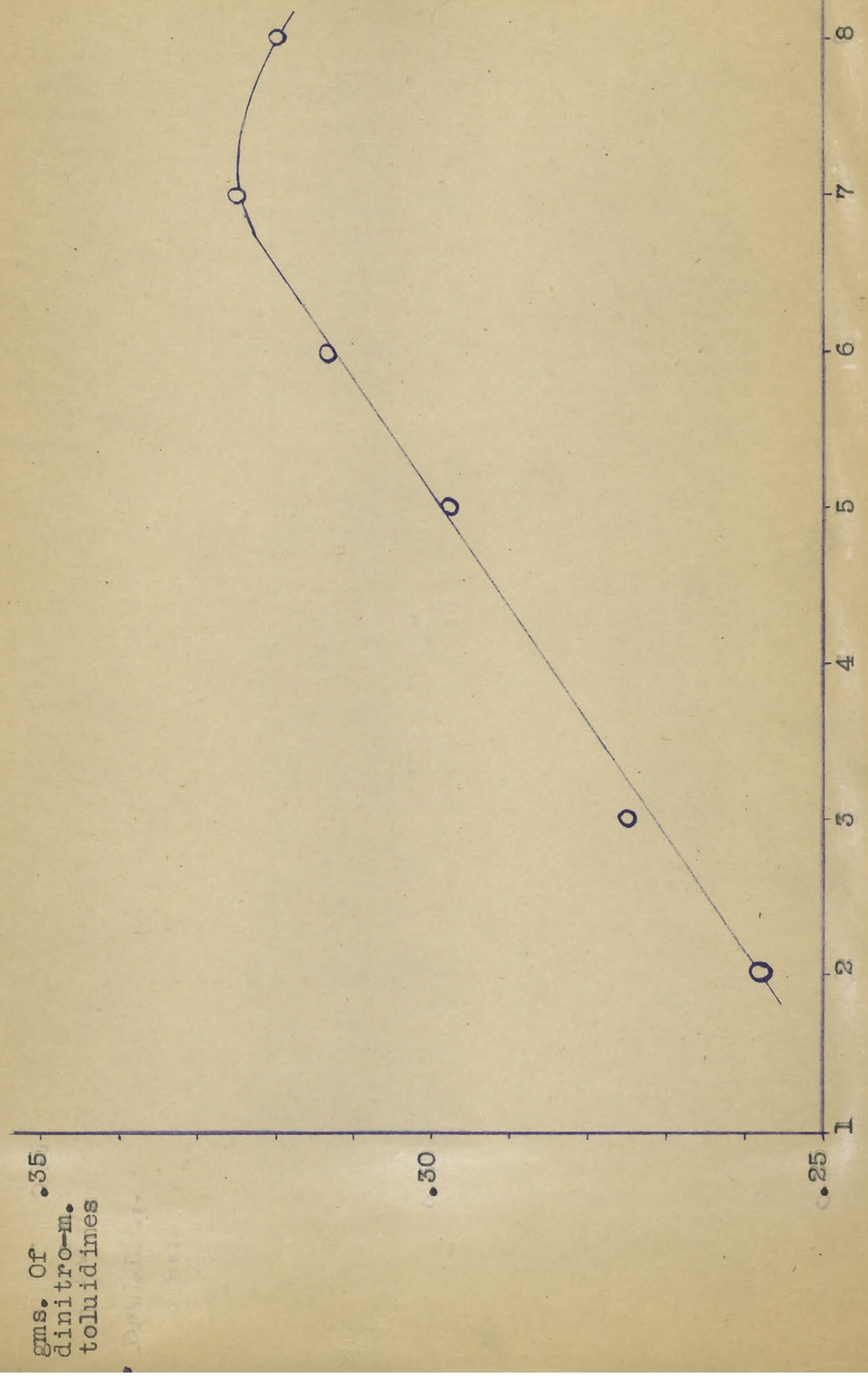
excess of alkali inhibits the amination completely. In this case, it is probable that the sodium dinitrotolyl-m-sulphonates react with the hydroxyl groups to give dinitro-m-cresols or their sodium salts. A solution was usually considered as sufficiently alkaline when it gave a faint blue coloration to litmus paper.

## II. Reaction time.

The determination of the optimum concentration of methylamine showed that, even if the reaction mixture had stood for 15 hours in the ice-box, a few hours (about 6) after filtration a second precipitate was formed which, under the circumstances, represented 12% of the total yield of dinitro-3-N-methyltoluidines.

In order to avoid the second precipitation, the following runs were carried out. The procedure previously used was slightly modified.

> In a closed reaction flask, a 50-ml. sample of slightly alkaline Sellite wash first liquor was treated with 0.594 gms. of methylamine. The solution was stirred at 45 - 50° C. for a certain length of time. When the reaction time was over, the mixture was cooled to room temperature and kept in the ice-box for another 15 hours. A second precipitation usually took place. The precipitates, filtered off on Gooch crucibles,



GRAPH 2

were rapidly washed with a small amount of cold distilled water and dried in a vacuum desiccator to constant weight.

The reaction time was different for each run and the following results were obtained.

TABLE III

| Run No. | Reaction time in hours | First pptate. in gms. | Second pptate. in gms. | Total Yield in gms. |
|---|---|---|---|---|
| 11 | 2 | 0.232 | 0.027 | 0.258 |
| 12 | 3 | 0.250 | 0.025 | 0.275 |
| 13 | 5 | 0.278 | 0.020 | 0.298 |
| 14 | 6 | 0.303 | 0.010 | 0.313 |
| 15 | 7 | 0.319 | 0.006 | 0.325 |
| 16 | 8 | 0.316 | 0.004 | 0.320 |

Run 16 was kept at room temperature instead of being placed in the ice-box for 15 hours. However, it is not possible to conclude from this run, and from others carried out under the same conditions, that room temperature is sufficient to insure complete precipitation as it happened that the room temperature referred to was as low as 15°C., but rather that a moderate cooling should suffice. It is believed that in an industrial plant, cooling by running water should be satisfactory.

## III. Optimum Temperature of Reaction

The temperature of reaction previously used had been arbitrarily chosen. To determine exactly which temperature was the most suitable, a few runs were carried out. At room temperature, the reaction proceeded very slowly: after 7 hours, nearly no reaction had occurred. After 16 hours, from 50 ml. of Sellite first solution, only 0.228 gms. of dinitro-3-N-methyltoluidines had precipitated. This temperature was evidently not suitable.

At temperatures varying from 60 to 75° C., even in a system closed by a mercury seal, the loss of methylamine was such that the concentration of this reagent in the reaction mixture decreased rapidly. The reaction proceeded rapidly, but the yield of substituted toluidines was appreciably lowered. The loss was about 32%.

TABLE IV

| Run No. | $CH_3NH_2$ in gms. | Temperature of Reaction ° C. | Reaction Time in hours | Volume of Sellite 1st in ml. | Yield in gms. |
|---|---|---|---|---|---|
| 17 | 0.594 | 25 | 7 | 50 | 0.093 |
| 18 | 0.594 | 45 - 50 | 7 | 50 | 0.319 |
| 19 | 0.594 | 70 - 75 | 7 | 50 | 0.216 |

It was concluded that the arbitrarily set temperature was, by mere chance, the only suitable one to give the results already mentioned.

## IV. Procedure of Amination

From the aforementioned experimental work, the following procedure was standardized and applied to all further preparations of dinitro-3 N-methyltoluidines.

> In a flask equipped with a mercury-sealed stirrer and a thermometer, a mixture of x ml. of slightly alkaline Sellite wash liquor was heated at 45-50°C. for seven hours with an amount of methylamine corresponding to 1.188 gms. per 100 ml. of liquor. When the reaction time was over, the mixture was cooled to room temperature and placed in the ice-box for 15 hours. The precipitate, separated by filtration, was washed with cold distilled water

and then dried in a desiccator. This procedure practically eliminates the second precipitation of toluidines.

## V. Composition of the Sellite Liquor

The industrial preparation of trinitrotoluene does not yield a crude material of constant composition. The concentration of unsymmetrical trinitrotoluenes in the crude nitration products is subject to appreciable fluctuation. In view of getting information on this question, a series of runs was carried out on first and second liquors of the sodium sulphite purifications obtained from Canadian Industries Limited trinitrotoluene plant at McMasterville, Que., from December 20th to 24th 1940. The following results were obtained.

Table V on Page 51.

## TABLE V

| Liquor of | Run No. | Sellite 1st yield in gms./litre | Run No. | Sellite 2nd yield in gms./litre |
|---|---|---|---|---|
| Dec. 20 | 20 | 3.37 | - | - |
| | 21 | 3.13 | - | - |
| " 21 | 22 | 4.78 | 30 | 13.55 |
| | 23 | 4.87 | 31 | 13.50 |
| " 22 | 24 | 6.36 | 32 | 15.92 |
| | 25 | 6.30 | 33 | 14.14 |
| " 23 | 26 | 6.71 | 34 | 12.64 |
| | 27 | 6.68 | 35 | 12.76 |
| " 24 | 28 | 7.39 | 36 | 18.55 |
| | 29 | 7.30 | 37 | 16.23 |

These runs were carried out about three weeks after the sampling of the liquor at the plant. Because of the lack of documentation on the quality of the above mentioned trinitrotoluene, it cannot be said whether the recorded variation in composition of the liquor is due to abnormal preparation, or caused by decomposition of the sodium dinitrotolyl-m-sulphonates on standing. This last hypothesis seems unlikely because liquors previously obtained had a decomposition corresponding to the liquors of December 20th and 21st.

The average yield of dinitro-3 N-methyltoluidines from the Sellite wash liquors is:

| | | |
|---|---|---|
| Sellite first | 5.689 | gms./litre |
| Sellite second | 14.66 | " " |
| Average | 10.17 | " " |

Samples of spent sodium sulphite liquors coming from Defence Industries Limited trinitrotoluene plant, Salaberry, Que., were submitted to the usual procedure of amination. A yield of 2.45 gms. of dinitro-3 N-methyltoluidines per litre of liquor was obtained.

B. Nitration of the Dinitro-3 N-Methyltoluidines

The amination of the spent liquors of the sodium sulphite purification gives a mixture of substituted toluidines in which the 2,4- and 2,6-dinitro-3 N-methyltoluidines form the major part. As both toluidines, once nitrated, give the same product, it was not necessary to do an elaborate separation of these isomers. The purpose of this research was to find an economical method of nitrating these substituted toluidines. Unfortunately, yields above 80% were never obtained probably on account of the low degree of purity of the starting material.

## I. Nitration in nitric acid.

The nitration of the 2,4- and 2,6-dinitro-3 N-methyltoluidines was studied by Brady and Gibson (18) during the last war and they concluded that in nitric acid alone the following procedure gave the best results.

> "40 grams of the toluidines are added in small quantities to 100 ml. of nitric acid, (d. 1.50) warmed at 50°C. Copious nitrous fumes are evolved. When all the solid has been added, the mixture is heated on the water bath until the evolution of nitrous fumes cease. The mixture is then cooled and water added. Usually the nitramine (XV) separates out as an oil which solidifies on keeping. The solid is washed thoroughly and crystallized from ethanol."

It must be noticed that in this procedure, no reaction time is given nor any dilution ratio at the end of the reaction time.

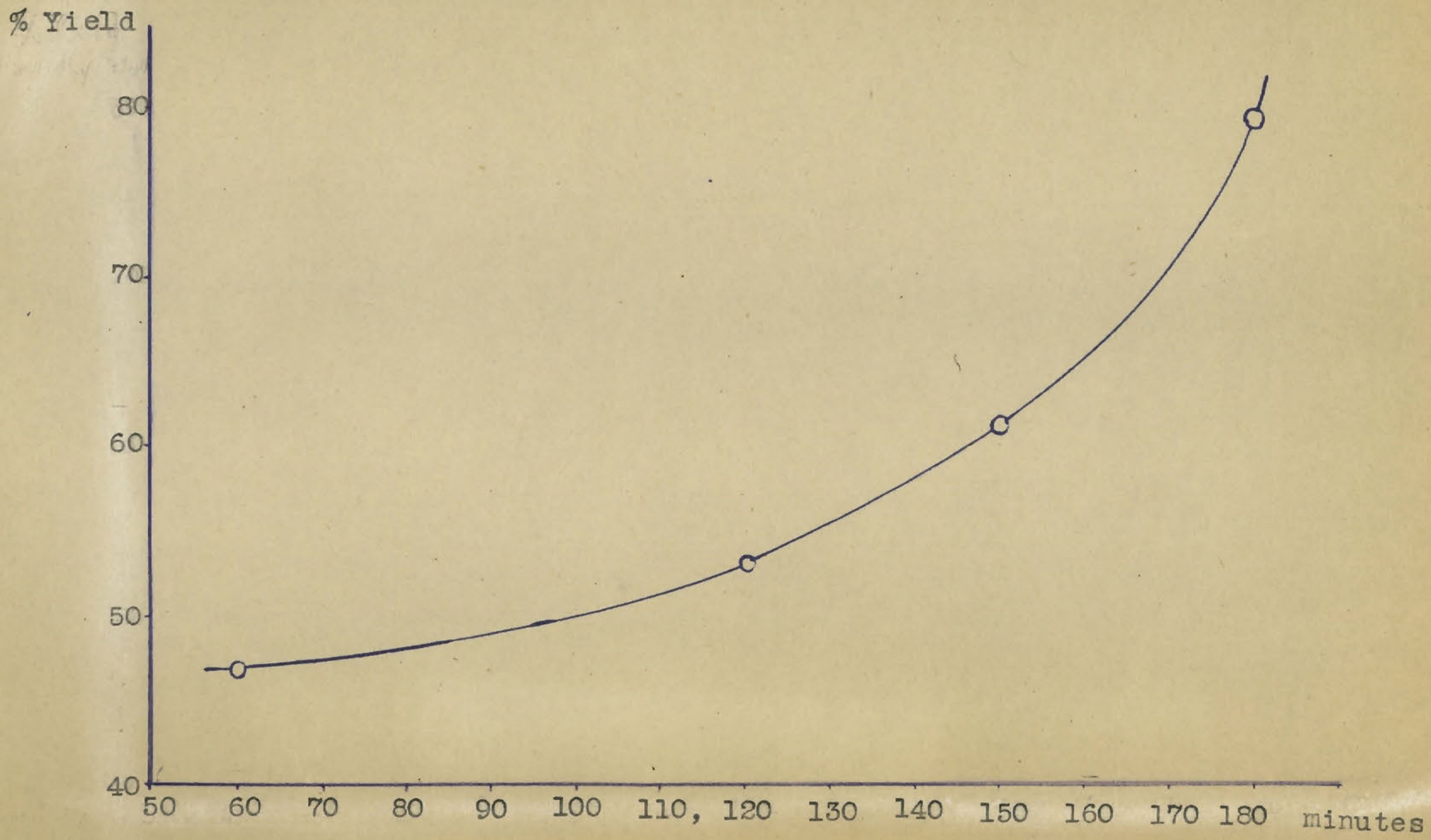
The procedure as described was used in many runs, but several difficulties were encountered. Runs were carried out in order to find the optimum dilution of nitration mixture after reaction. It was found that a ten-fold dilution was necessary. Furthermore, to prevent the separation of the product as an oil, cooling in an ice bath was necessary. Otherwise, with a lower dilution and no cooling, the nitramine (XV) was incompletely precipitated and the diluted spent acid held some nitramine in very fine suspension which settled down very slowly (over 24 hrs.).

These points having been determined, runs were carried out to find the maximum yields that could be obtained by Brady and Gibson's procedure. The crude nitramine was dissolved in boiling ethanol from which it crystallized on cooling. The results obtained are summarized in Table VI (graph III).

Table VI on page 55.

## TABLE VI

| Run | Dinitro-3 N-Methyl-Toluidines mole | $HNO_3$ |  | Excess of $HNO_3$ | Addition |  | Reaction |  | Product of Nitration |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | gms. | % | % | Temp. °C. | Time Mins. | Temp. °C. | Time Mins. | gms. | M.P. °C | Yield % |
| 1 | 0.047 | 37.5 | 92 | 489.5 | 50 | 20 | 90 - 100 | 60 | 6.7 | 100 - 101 | 47 |
| 2 | 0.047 | 37.5 | 92 | 489.5 | 50 | 20 | 90 - 100 | 120 | 7.55 | 100 - 101 | 53 |
| 3 | 0.047 | 37.5 | 92 | 489.5 | 50 | 20 | 90 - 100 | 150 | 8.755 | 100 - 101 | 61.2 |
| 4 | 0.047 | 37.5 | 92 | 489.5 | 50 | 20 | 90 - 100 | 180 | 11.293 | 99 - 100 | 79.1 |


% Yield
80
70
60
50
40
50
60
70
80
90
100
110,
120
130
140
150
160
170
180
minutes

GRAPH 3.

Under the conditions given above, the reaction time seems to be a controlling factor. The amount of nitric acid used compared with the theoretical amount required by the reaction is enormous. It was attempted to reduce this excess of nitric acid. Many difficulties were encountered. It was impossible to decrease the excess of nitric acid below 60% because there was not enough liquid to dissolve the required amount of toluidines. No m-methyltetryl was formed unless a 78.5% excess of nitric acid was used. With this excess it was attempted to vary the temperature and the reaction time, but no better yields than 30% were ever obtained. (Run 9). It was then tried, with a larger excess of acid to reverse the mode of addition; (runs 10, 11 and 12) the acid was added to the toluidines. The only advantage here was to decrease the time of addition and, when the reaction was carried out at a temperature of 40-50° C., it decreased the loss of nitric acid (fuming off). No real advantage results from the reverse conditions. From these experiments summarized in Table VII, no really good yields were obtained but it was shown that the 489.5% excess is indispensable and that the conditions of reaction established by Brady and Gibson are the only ones that can be used in the nitration of the 2,4- and 2,6 dinitro-3 N-methyltoluidines by fuming nitric acid alone.

## TABLE VII

| Run No. | Excess of $HNO_3$ % | Final Conc. $HNO_3$ % | Mole of dinitro-methyltoluidines | $HNO_3$ % | $H_2O$ % | $HNO_3$ gms. | $HNO_3$ % | Addition Temp. °C. | Addition Time Mins. | Reaction Temp. °C. | Reaction Time Mins. | Products First crop gms. | Products First crop M.P. | Yield % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | 78.5 | 60 | 0.05 | 92 | 8 | 11.25 | 92 | 15 | 30 | 15 | 30 |  | Tars | .. |
| 6 | 78.5 | 60 | 0.05 | 92 | 8 | 11.25 | 92 | 15 | 30 | 50 | 30 | 2.3 | 153-154 |  |
| 7 | 78.5 | 60 | 0.05 | 92 | 8 | 11.25 | 92 | 15 | 30 | 65 | 30 |  | Tars | .. |
| 8 | 78.5 | 60 | 0.05 | 92 | 8 | 11.25 | 92 | 15 | 30 | 90 | 30 | 4.4 | 92-100 | 30 |
| 9 | 98.4 | 65 | 0.05 | 92 | 8 | 12.5 | 92 | 20 | 5 | 90 | 55 | 6.4 | 95-96 | 42.5 |
| 10 | 98.4 | 65 | 0.05 | 92 | 8 | 12.5 | 92 | 20 | 5 | 90 | 115 | 5.75 | 95-96 | 39 |
| 11 | 98.4 | 65 | 0.05 | 92 | 8 | 12.5 | 92 | 20 | 5 | 90 | 30 | 5.02 | 95-96 | 33 |

## Nitration in mixed acids.

The nitration in fuming nitric acid is rather an expensive process and, on account of the high dilution of the spent acid, no recovery is economically possible. To overcome this difficulty, it was attempted to nitrate the dinitro-3-N-methyltoluidines in mixed acids. The procedure of nitration is completely different from Brady and Gibson's (18). In this case, the toluidines could be added to the reaction mixture in three different ways: either added to the mixed acids, dissolved in sulphuric acid alone (adding nitric acid when the solution is completed) or dissolved in a mixture of sulphuric and nitric acids, bringing the mixture to the required composition by adding sulphuric and nitric acids as needed. All these were tried in different runs, and, using a small excess of nitric acid, the dehydrating value of sulphuric acid (D.V.S.) (44) was varied.

To start with, a run was carried out using a D.V.S. of 6.2 and an excess of nitric acid of 9.7%, giving a final concentration of 0.9% of this acid after nitration. The toluidines were added to the mixed acids at 80°C. over a period of 30 minutes. When the addition was completed, the mixture was stirred at 100°C. for one hour. Then, the reaction mixture was diluted with ice. 0.01 mole of toluidines yielded 1.179 gms. or 39.1% of m-methyltetryl, crystallized from ethanol, m.p. 100°C.

In lowering the D.V.S. to 5 and, by the way, the excess and final concentration of nitric acid, and decreasing the temperature of addition to 50° C., and the reaction temperature to 80° C., a 48.1% yield was obtained. No improvement was obtained below these conditions. Using the same time and temperature for addition and subsequent reaction, no m-methyltetryl was obtained when a lower excess of nitric acid was used. The material obtained from this last nitration was believed to be the 2,4-dinitrotolyl-3-methylnitramine. Brady and Gibson give for such a compound a melting point of 111°C. and the material obtained, after crystallization from alcohol, melted at 110-111° C.

Results are shown in Table VIII.

Table VIII on page 60.

## TABLE VIII

| Run No. | D.V.S. | Excess of $HNO_3$ % | Final Conc. $HNO_3$ % | Mole of Dinitro-m-methyltoluidines | $HNO_3$ % | $H_2SO_4$ % | $H_2O$ % | $HNO_3$ gms. | $HNO_3$ % | $H_2SO_4$ gms. | $H_2SO_4$ % | Addition Temp. °C. | Addition Time mins. | Reaction Temp. °C. | Reaction Time mins. | Product gms. | Product M.P. | Yield % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | 6.2 | 9.7 | 0.9 | 0.01 | 14.98 | 76.7 | 8.32 | 1.92 | 70 | 7.247 | 95 | 80 | 30 | 100 | 60 | 1.178 | 100° | 39.1 |
| 13 | 5 | 5 | 0.89 | 0.01 | 16.22 | 73.4 | 10.44 | 1.85 | 70 | 6.32 | 95 | 50 | 25 | 80 | 60 | 2.9 | 100-101 | 48.1 |
| 14 | 4.7 | 5 | 0.96 | 0.01 | 17.5 | 72 | 10.5 | 1.85 | 70 | 5.77 | 95 | 50 | 15 | 85 | 25 | 2.83 | 100-101 | 47. |

In the preceding runs, the temperature seemed to be too high especially with a D.V.S. of 6.2. A few runs (15 - 18) were carried out at low temperatures using a D.V.S. of approximately 10. The toluidines were dissolved in sulphuric acid and when the dissolution was completed, a mixture of nitric and sulphuric acids was added slowly to complete the required acid mixture. As indicated in a following table, when the addition was done below 0°C. the reaction did not seem to proceed properly. Above 0°C. the yield decreased as the time and the temperature of addition and reaction increased. Table IX covers the above mentioned series. It was thus concluded that low temperature favoured the reaction.

(See Table IX on page 62.)

In using analogous conditions, but a lower D.V.S. and a higher nitric acid excess, higher yields were obtained. Table X and graph IV illustrate the variation of the yield of m-methyl tetryl in function of the reaction temperature.

(See Table X on page 63.)

TABLE IX

| Run No. | D.V.S. | Excess of $HNO_3$ % | Final Conc. $HNO_3$ % | Mole of dinitro-3 m-methyl-toluidines | $HNO_3$ % | $H_2SO_4$ % | $H_2O$ % | $HNO_3$ | | $H_2SO_4$ | | Addition | | Reaction | | Product | | | | Yield |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | gms. | % | gms. | % | Temp. °C. | Time mins. | Temp. °C. | Time mins. | gms. | M.P. °C. | gms. | M.P. °C. | % |
| 15 | 9.81 | 5 | 0.31 | 0.05 | 6 | 87 | 7 | 9.2 | 72 | 97.5 | 95 | 15 | 60 | 0 | 180 | 5.79 | 99-100 | | | 38.4 |
| 16 | 9.81 | 5 | 0.31 | 0.05 | 6 | 87 | 7 | 9.2 | 72 | 97.5 | 95 | 0 | 60 | 0 | 60 | 7.54 | 99-100 | 1.49 | 90-95 | 60 |
| 17 | 10.3 | 4.5 | 0.44 | 0.05 | 8.8 | 83.3 | 7.9 | 9.145 | 72 | 65.6 | 95 | 15 | 30 | 50 | 20 | 7.58 | 99.5 | | | 50.3 |
| 18 | 10.3 | 4.5 | 0.44 | 0.05 | 8.8 | 83.3 | 7.9 | 9.145 | 72 | 65.6 | 95 | 15 | 60 | 50 | 60 | 7.2 | 99.5 | | | 47.7 |

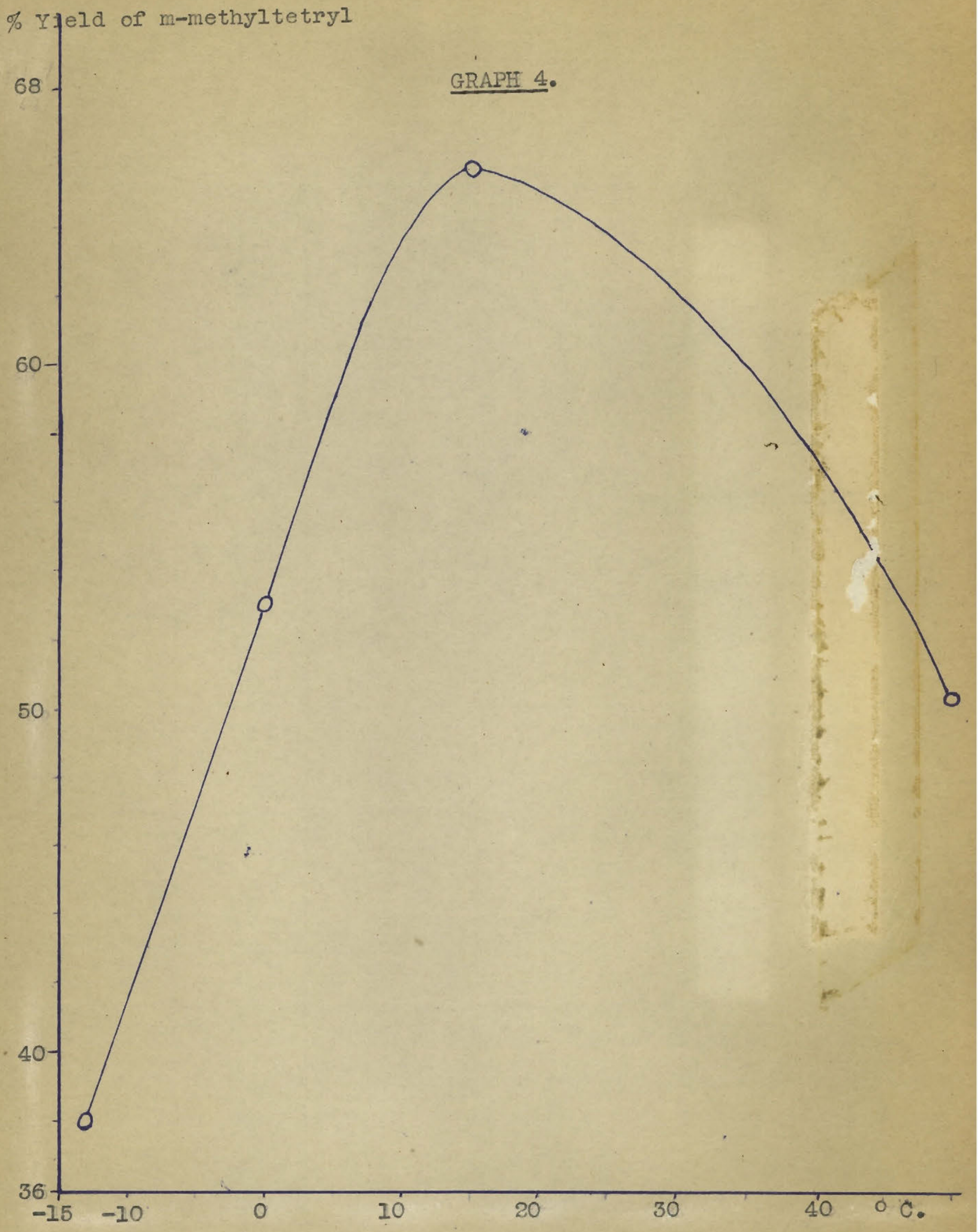

% Yield of m-methyltetryl
GRAPH 4.
68
60
50
40
36
-15
-10
0
10
20
30
40
° C.

TABLE X

|  |  |  |  |  |  |  |  |  |  | Addition |  | Reaction |  | Product |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  |  |  |  |  |  | 1st Crop |  | 2nd Crop |  | Yield |
| Run | D.V.S. | Excess $HNO_3$ % | Final Conc. $HNO_3$ % | Mole of Dinitro-3 m-methyl-toluidines | $HNO_3$ % | $H_2SO_4$ % | $H_2O$ % | $HNO_3$ gms. | % | Temp. °C. | Time mins. | Temp. °C. | Time mins. | gms. | M.P. °C. | gms. | M.P. °C. | % |
| 19 | 5.8 | 312.7 | 28.5 | 0.05 | 33 | 58.7 | 8.3 | 26 | 92 | - 5 | 60 | - 13 | 60 | 4.31 | 100-101 | 1.4 | 94-95 | 38 |
| 20 | 5.8 | 312.7 | 28.5 | 0.05 | 33 | 58.7 | 8.3 | 26 | 92 | 0 | 60 | 0 | 60 | 7.01 | 99-100 | 0.96 | 92-95 | 53 |
| 21 | 5.8 | 312.7 | 28.5 | 0.05 | 33 | 58.7 | 8.3 | 26 | 92 | 0 | 60 | 15 | 60 | 8.62 | 99-100 | 1.26 | 94-96 | 65.7 |
| 22 | 5.8 | 312.7 | 28.5 | 0.05 | 33 | 58.7 | 8.3 | 26 | 92 | 15 | 60 | 50 | 60 | 7.57 | 99-100 | .. | .. | 50.3 |

Increasing the excess of nitric acid did not seem to influence the reaction appreciably (runs 19 - 22) as the results obtained were about the same as those indicated in Table X. Attempts were made to use a lower excess of nitric acid and mixed acids analogous to those used in the preparation of tetryl (43). One run (23) was carried out in acids of a high D.V.S. and with a 142.8% excess of nitric acid. The reaction was carried out at low temperature and a 64.1% yield was obtained. In subsequent runs (24 - 25), for $H_2SO_4$ only, the reverse was tested; a low D.V.S. and a 203.4% excess of nitric acid were used. In the first run, the addition of the toluidines to the mixed acids was done at 0°C. and the reaction time after addition was 60 minutes at 40°C.; in the second run, the addition was done under the same conditions, but the reaction time was increased by half an hour. The first run gave a 58% yield while the second gave 64.6%.

In another attempt to us mixtures of acid already used in the explosive industry, runs were made (26 - 27) using mixed acids which are already used in the Salaberry tetryl plant of Defence Industries Limited; this mixture had a D.V.S. of 5.2 when a 270% excess of nitric was used. These runs, carried out under different conditions gave 58.4 and 70% yield. Results and reaction conditions are summarized in Table XI.

## TABLE XI

| Run No. | D.V.S. | Excess of $HNO_3$ % | Final conc. $HNO_3$ % | Mole of dinitro-3 m-methyl toluidines | $HNO_3$ % | $H_2SO_4$ % | $HNO_3$ | | $H_2O$ % | $H_2SO_4$ | | Addition | | Reaction | | Product | | | | Yield % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | | | 1st Crop | | 2nd Crop | | |
| | | | | | | | gms. | % | | gms. | % | Temp. °C. | Time Mins. | Temp. °C. | Time Mins. | gms. | M.P. °C. | gms. | M.P. °C. | |
| 23 | 8.1 | 142.8 | 13.8 | 0.025 | 23.08 | 71.7 | 8.5 | 92 | 5.22 | 26.36 | 95 | 0 | 15 | 0 | 120 | 3.9 | 98-99 | 0.92 | 94-96 | 64. |
| 24 | 4.14 | 203.49 | 19.04 | 0.025 | 27.4 | 60.5 | 10.3 | 92 | 11.9 | 22.2 | 95 | 0 | 15 | 40 | 60 | 3.68 | 99-100 | 0.75 | 97-98 | 58. |
| 25 | 4.14 | 203.49 | 19.04 | 0.05 | 27.4 | 60.5 | 20.6 | 92 | 11.9 | 44.4 | 95 | 0 | 15 | 40 | 90 | 7.8 | 99-100 | 1.9 | 98-99 | 64.6 |
| 26 | 5.2 | 270 | 39.8 | 0.025 | 28.4 | 28.4 | 16.9 | 70 | 13.52 | 40.8 | 95 | 25 | 60 | 45 | 30 | 4.5 | 100-101 | .. | .. | 58.4 |
| 27 | 5.2 | 270 | 23.8 | 0.025 | 50.04 | 45.4 | 12.3 | 92 | 4.975 | 11.35 | 95 | 15 | 15 | 40 | 120 | 3.5 | 91-100 | 9.75 | 98-99 | 70. |

Runs 26 and 27 can hardly be compared on account of the difference in conditions of temperature and reaction time.

Another group of nitrations was carried out using a mixed acid commonly known at any explosive plant as "antifreeze-mixture" and having the following composition:

| | |
|---|---|
| $HNO_3$ | 84.5% |
| $H_2SO_4$ | 12.2% |
| $H_2O$ | 3.3% |

The following procedure was followed when using this mixture:

> The toluidines were dissolved in the mixed acids. The addition time and temperature were 20°C. and 15 minutes while the reaction time was 30 minutes at temperatures varying between 40 and 60°C. In the first two runs, the reaction mixture, after nitration, solidified on cooling. In order to eliminate the spent acids, the solids were made into a slurry with a small amount of sulphuric acid. In the other runs, even on cooling, no solidification ever occurred, but a viscous liquid was formed. However, the addition of cold sulphuric to the viscous oil precipitated complete-

ly the m-methyltetryl formed. The amount of sulphuric acid required to crystallize the nitration product increased with the increasing excess of nitric acid.

Table XII shows the results obtained.

(See Table XII on page 68.)

This procedure has the great advantage of eliminating the dilution of the spent acids with water. It seems that the 700% excess gives the optimum concentration of acids and as the results indicate, the temperature does not affect the yield.

## C. Conclusion

The dinitro-3-N-methyltoluidines can be nitrated to m-methyltetryl by different procedures. It should be noticed that the starting material is nitrated without previous purification and, according to the process of nitration, the reaction yields from 60 to 80% of nitramine (XV). A short summary of these procedures, established from the previously described experimental nitration, is given below.

### I. Nitration in fuming nitric acid.

The nitration of the dinitro-3-N-methyltoluidines carried out with fuming nitric acid can be successfully

## TABLE XII

| Run No. | D.V.S. | Excess of HNO % | Final conc. HNO % | Mole of dinitro-3 m-methyl toluidines | Anti-freeze mixture gms. | Addition | | Reaction | | $H_2SO_4$ added gms. | Product 1st Crop | | Product 2nd Crop | | Yield % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Temp. °C. | Time Mins. | Temp. C. | Time mins. | | gms. | M.P. °C. | gms. | M.P. °C. | |
| 28 | 0.7 | 98.5 | 60 | 0.025 | 7.4 | 20 | 15 | 40 | 30 | 9.20 | 3.3 | 98 | .. | .. | 44 |
| 29 | 0.7 | 98.5 | 60 | .. | 7.4 | 20 | 15 | 60 | 30 | 9.2 | 3.3 | 97-98 | .. | .. | 44 |
| 30 | 1.02 | 181.6 | 70 | .. | 10.5 | 20 | 15 | 40 | 30 | 36.8 | 3.7 | 98-99 | 0.8 | 95-96 | 60 |
| 31 | 1.02 | 181.6 | 70 | .. | 10.5 | 20 | 15 | 60 | 30 | 36.8 | 2.8 | 98-99 | 1.6 | 93-94 | 58.6 |
| 32 | 1.3 | 704.7 | 81.7 | .. | 30 | 20 | 15 | 40 | 30 | 64.08 | 2.7 | 99.5 | 2.4 | 93-94 | 68 |
| 33 | 1.3 | 704.7 | 81.7 | .. | 30 | 20 | 15 | 60 | 30 | 64.08 | 4.2 | 100-101 | 0.9 | 97-98 | 68 |
| 34 | 7.12 | 884.5 | 87.7 | .. | 36.7 | 20 | 15 | 60 | 30 | 82.8 | 4.83 | 99 | .. | .. | 64.5 |

done by Brady and Gibson's procedure (18). The ten-fold dilution of the reaction mixture and the moderate cooling will insure a yield as high as 79%.

II. Nitration in mixed acids.

When the nitration is carried out in mixed acids, two important factors are the temperature and the excess of nitric acid.

a) Low-temperature nitration:

(i) With 5% excess of nitric acid

Under these conditions, the procedure of nitration can be described as follows:

0.05 of a mole of toluidines is dissolved into 55 gms. of 95% sulphuric acid. The temperature is kept constant (20°C.) by cooling with running water. When the dissolution is completed, the solution is cooled at 0°C. and a mixture of 42.5 gms of 95% sulphuric acid and 9.2 gms. of 70% nitric acid is added over a period of one hour. When the addition is completed, the reaction is kept at this temperature for another hour. Then, the solids formed are filtered off on glass wool. The crude m-methyltetryl obtained is thoroughly washed with cold water until free from acid and then dissolved in boiling ethanol from which it crystallizes on cooling. The mother liquor, on evaporation gives another crop of crystals of low melting points.

Composition of the mixed acids:

| | | |
|---|---|---|
| | $H_2SO_4$ | 87% |
| | $HNO_3$ | 6% |
| | $H_2O$ | 7% |
| D.V.S. | | 9.81 |
| Yield, in gms. | | 7.54 m.p. 99-100°C. (corr.) |
| | | 1.49 m.p. 90-95°C. (corr.) |
| Overall yield | | 60% |

(ii) With 142.8% excess nitric acid

When this excess is used, the procedure of nitration is somewhat the reverse of the preceding one. The toluidines are dissolved in the nitric acid instead of in the sulphuric acid. The solubility of the dinitro-3-N-methyltoluidines in nitric acid is much greater than in sulphuric acid so that the dissolution is more rapid in nitric acid than it is in sulphuric acid.

Procedure:

0.025 of a mole of substituted toluidines is dissolved in 8.5 gms. of ice-cold 92% nitric acid. Then, 23.36 gms. of 95% sulphuric acid is added over a period of 15 minutes at 0°C. The reaction mixture is kept at 0oC. for two hours after which it is cooled in an ice and salt bath for 20 minutes to complete the crystallization of the m-methyltetryl which is filtered off on glass wool. The spent acids on dilution give a small amount

of oily material which does not crystallize.
The solids are washed free from acid and crystallized from ethanol.

Composition of the mixed acids:

| | |
|---|---|
| $H_2SO_4$ | 71.7% |
| $HNO_3$ | 23.08% |
| $H_2O$ | 5.22% |
| D.V.S. | 8.1 |
| Yield, in gms. | 3.9 m.p. 98-99° C. (corr.) |
| | 0.92 m.p. 94-96° C. (corr.) |
| Overall yield | 64.1% |

(iii) With 203.5% excess of nitric acid.

The nitration of the dinitro-3-N-methyltoluidines with this excess of nitric acid is carried by the following procedure:

In mixed acids formed of 10.4 gms. of 92% nitric acid, 22.2 gms. of 95% sulphuric acid and 3.3 gms. of water, cooled at 0°C., 0.025 of a mole of toluidines is dissolved over a period of 15 minutes. The mixture is then heated slowly at 40°C. and kept at this temperature for 1 1/2 hours. The nitration mixture, in which m-methyltetryl has already started to crystallize, is cooled in an ice bath then the solids are filtered off, washed with water until free from acid and crystallized from ethanol. The spent acids are diluted with water and the solids are added to the first precipitate for crystallization from alcohol.

Composition of the mixed acids:

| | |
|---|---|
| $H_2SO_4$ | 60.5% |
| $HNO_3$ | 27.4% |
| $H_2O$ | 11.9% |
| D.V.S. | 4.14 |
| Yield, in gms. | 7.8 m.p. 99-100°C. |
| | 1.9 m.p. 98-99°C. |
| Overall yield | 64.6% |

b) Medium temperature of nitration

In the procedure described below, the reaction is carried out at a temperature of 40°C.

An excess of nitric acid of 270% is used as in the preparation of tetryl from dimethylaniline. The toluidines are treated as follows:

Procedure:

In a mixture of 12.3 gms. of 92% nitric and and 11.35 gms. of 95% sulphuric acid, 0.025 of a mole of toluidines is dissolved at a temperature of 15°C. over a period of 15 minutes. The temperature is then raised to 40°C. After two hours at this temperature, the nitration products are crystallized out by cooling in an ice and salt bath. The crude m-methyltetryl is filtered off, washed with water and crystallized from alcohol. The spent acids, diluted with water (equal volume) give a residue which is crystallized from alcohol with the m-methyltetryl previously obtained.

Composition of the acid mixture:

| | | |
|---|---|---|
| | $H_2SO_4$ | 45.4% |
| | $HNO_3$ | 50.04% |
| | $H_2O$ | 4.97% |
| D.V.S. | | 5.2 |
| Yield, in gms. | | 3.5 m.p. 99-100° C. (corr.) |
| | | 1.75 m.p. 98-99° C. (corr.) |
| Overall yield | | 70%. |

### III. Nitration in mixed acids of low sulphuric acid concentration.

The following procedure was elaborated in order to eliminate the dilution of spent acids with water. The mixed acids used are the standard anti-freeze mixture of nitric and sulphuric acid well known in the explosives industry. The procedure can be described as follows:

In 30 gms. of anti-freeze mixture, 0.025 of a mole of dinitro-toluidines is dissolved at room temperature (20°C.) over a period of 15 minutes. The mixture is then heated at 60°C. for half an hour after which it is cooled in an ice and salt bath. To obtain crystallization, the cold reaction products are diluted with 64.08 gms. of sulphuric acid (sp. gr. 1.84). The crystals are washed with water until free from acid and crystallized from ethanol.

Composition of the mixed acids:

| | | |
|---|---|---|
| | $H_2SO_4$ | 84.5% |
| | $HNO_3$ | 12.5% |
| | $H_2O$ | 3.3% |
| D.V.S. | | 1.3 |
| Excess of nitric acid | | 704.7% |
| Yield in gms. | | 4.2 m.p. 100-101°C. (corr.) |
| | | 0.9 m.p. 97-98°C. (corr.) |
| Overall yield | | 68.0% |

The procedures described herein are, as far as the writer is concerned, those giving the best yields; it is not within the scope of this study to determine which method of nitration would be the most efficient and economical.

## DISCUSSION OF RESULTS

The nitration of the purest toluene available gives 95.5% of 2,4,6-trinitrotoluene and 4.5% of unsymmetrical isomers in the laboratory (19), but at the trinitrotoluene plant of Canadian Industries Ltd., McMasterville, Que., the yield of trinitrotoluene is only 80%. The amount of unsymmetrical trinitrotoluenes produced at this factory is unknown, but it is assumed that they represent 4.5% of the crude explosive. As each 2,600-lb. batch of crude trinitrotoluene is treated with 8,000 lbs. of sodium bisulphite solution divided in two washes, it is possible to evaluate the amount of unsymmetrical isomers that are dissolved in the Sellite wash waters. Since from experimental results it was found that 1 litre of Sellite wash liquor gives 10.17 gms. of dinitro-3-N-methyltoluidines and the specific gravity of the Sellite wash water if 1.021 ($22^oC.$) then the amount of dinitro-3-N-methyltoluidines available from one batch of trinitrotoluene is 79.6 lbs. A ton of trinitrotoluene gives 61.2 pounds of dinitro-3-N-methyltoluidines.

Assuming that the amination of the sodium dinitrotolyl-m-sulphonates proceeds to 100%, it is possible to evaluate the amount of unsymmetrical trinitrotoluene present in the crude nitration product. As one ton of trinitrotoluene yields 61.2 pounds of dinitro-3-N-methyltoluidines, the corresponding amount of unsymmetrical trinitrotoluenes is 65.8 lbs., of 3.2%

The nitration of the dinitro-3-N-methyltoluidines gives a yield that varies with the procedure. Assuming that the procedure used gives a 70% yield of m-methyltetryl (as in run 27) then, one mole of 0.465 lb. of toluidines gives 0.465 lb. of m-methyltetryl. As stated before, 1 ton of crude trinitrotoluene gives 61.2 lbs. of dinitro-3-N-methyltoluidines or 61.2 lbs. of nitramine. From these figures, 32.6 tons of crude trinitrotoluene would give 1 ton of m-methyltetryl.

It is very important to note that the yearly production of trinitrotoluene in Canada is 36,000 tons and in the United States will shortly be about a million tons. Under such circumstances, the possible production of m-methyltetryl, by this process, would be 31,779 tons a year. With this production, the booster mixture tetryl-trinitrotoluene could be replaced completely.

## STRUCTURE AND PROPERTIES

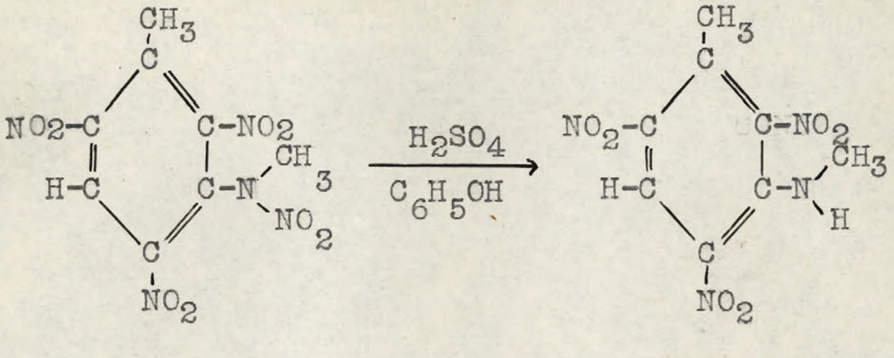
### Analysis and Structure Proof

Nitrogen determinations have been carried out on the 2,4,6-trinitrotolyl-3-methylnitramine by the Allen and Young (47) modified semi-micro Dumas combustion method. The following results were obtained.

Analysis:

| | |
|---|---|
| Calcd. for $C_8H_7O_8N_5$: | N, 23.22% |
| Found: | 23.33%<br>23.43% |

The structure of m-methyltetryl was studied by a reaction characteristic for this type of compound, the denitration of the amino group. The 2,4,6-trinitrotolyl-3-methylnitramine should give the 2,4,6-trinitro-3-N-methyltoluidine (XVII). The reaction was carried out according to a denitration method given by Houben (48) and a material melting at 130-134°C. was isolated. According to Houben, the 2,4,6-trinitro-3-N-methyltoluidine melts at 129.5°C. Blanksma (21), who synthesized m-methyltetryl from this substituted methyltoluidine, gives his melting point as 130°C. The trinitromethyltoluidine, after several recrystallizations, melted sharply at 134°C.



XVII

Action of Alkalies

In their investigation of 2,4,6-trinitrotolyl-3-methylnitramine, Brady and Gibson (18) mention that the nitramine is very sensitive towards alkalies. An alcoholic solution of m-methyltetryl gives with alkali an intense violet coloured complex. It is noteworthy that the nitramine is so sensitive that when recrystallized in glass vessels, the alkali of the glass is sufficient to affect it, if the solvent is not made slightly acid. The nitramine, once affected by alkalies, will have a grayish colour.

Solubility

m-Methyltetryl is slightly soluble in concentrated sulphuric acid, but very soluble in concentrated nitric acid; very slightly soluble in carbon tetrachloride and petroleum ethers, slightly soluble in alcohols such as ethanol and methanol, but very soluble in chloroform, benzene, acetone and acetic acid.

It is possible, using acetone or acetic acid as solvent, to recrystallize the nitramine by preparing a concentrated solution in one of these two solvents and then diluting with water to bring about crystallization. With a 20% solution of m-methyltetryl in 99.9% acetic acid, on bringing the concentration of the acid to 50% by adding water, 93% of the dissolved material crystallized as fine white heavy crystals. This peculiarity is very important, since the density of an explosive is never too great. Acetone is also a very good solvent, but, when dissolved in it, the nitramine tends to come out of solution as an oil which, on standing, gives a pale yellow solid. However, a solution of m-methyltetryl in either of these two solvents will, on extreme dilution with water, give white flakes of very pure nitramine, m.p. 101-102°C.

## Explosive properties.

The explosive properties of m-methyltetryl have not been completely investigated. From ballistic mortar experiments, it was found that its explosive force is 10% stronger than trinitrotoluene, but 16% weaker than tetryl (49). Its sensitivity is not greater than tetryl.

The methyl tetryl is a stable explosive. As there are no specifications concerning the stability of of m-methyltetryl, attempts to establish them were made. The nitramine used in these experiments, had been recrystallized three times. Samples recrystallized from different solvents were also used. It was found that m-methyltetryl will stand a temperature of 70.9°C. for at least 23 minutes in the Abel Heat Test (50).

To complete the investigation on the stability of this explosive, vacuum stability tests (52) were carried out at 100°C. on material crystallized from ethanol, acetic acid and acetone. Using the last solvent, it is not possible to obtain good white crystals within economical limits of dilution of acetone. When a 50% dilution is used, a yellow m-methyltetryl, m.p. 99.5°C. is obtained.

The results are summarized in Table XIV.

TABLE XIV

| Solvent | M.P. °C. | Colour | Vacuum Stability ml. of gas evolved at 100°C. |
|---|---|---|---|
| Ethanol | 101-102 | white | 0.38 - 0.42 |
| Acetic acid | 101-102 | white | 0.90 - 1.08 |
| Acetone | 101-102 | white | 0.65 - 0.69 |
| Acetone | 99.5 | yellow | 2.44 |

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