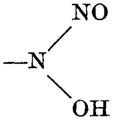
SOME ASPECTS OF THE CHEMISTRY OF NITRAMINES

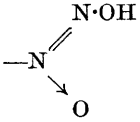
By ALEX. H. LAMBERTON, B.SC., PH.D.
(LECTURER IN CHEMISTRY, UNIVERSITY OF SHEFFIELD)

THE nitramines and nitramides are a well-defined group of organic compounds, whose common feature is to be found in their relationship to nitric acid. They may best be defined as amides of nitric acid, and the inorganic nitramine (I ; $R = R' = H$) may be regarded, formally, as the parent substance of the group. When, formally, one of the hydrogen atoms of nitramine is replaced by an alkyl group, one has a primary nitramine. In the secondary nitramines two alkyl groups are linked to nitrogen. In primary nitramides the substituents are hydrogen and an acyl group, and in the secondary (or alkyl-) nitramides the remaining hydrogen has been replaced by an alkyl group. These relationships, which are unaltered by the substitution of aryl for alkyl, are conveniently exhibited in Table I. These structures and the possibilities of tautomerism are discussed later.

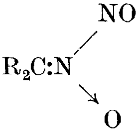
O-Alkyl derivatives of primary nitramines are known ; *e.g.*, (VI), b.p. 112°/760 mm., isomeric with dimethylnitramine. Though only one example (isomeric with the last compound of Table I) has yet been isolated, it seems likely that *O*-alkyl derivatives of the primary nitramides are in general capable of existence.[1] No compounds of the formula (I ; $R = R' = \text{Acyl}$) have been reported, and dinitro-compounds [$R{\cdot}N(NO_2)_2$] are likewise unknown. The nitrosohydroxylamino-group



or



is isomeric with the nitramino-group, but there is no evidence that nitrosohydroxylamines and nitramines are in any way interconvertible ; and the chemistry of the nitrosohydroxylamines will not be discussed.

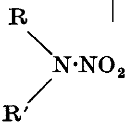
By the action of nitrous acid or dinitrogen tetroxide (N_2O_4) on the oximes of mesityl oxide and of a number of terpenoid ketones, compounds of the empirical formula $R_2CN_2O_2$ are produced. These have been variously formulated as $R_2C(NO)_2$, $R_2C{:}N{\cdot}O{\cdot}NO$, , or as the “ nitrimine ” $R_2C{:}N{\cdot}NO_2$. J. W. Suggitt, G. S. Myers, and G. F. Wright,[2] who review the earlier literature, have succeeded in condensing nitramine with furfuraldehyde (but not with other aldehydes) to yield the *N*-nitroaldimine by the equilibrium : $C_4H_3O{\cdot}CHO + NH_2{\cdot}NO_2 \rightleftharpoons C_4H_3O{\cdot}CH{:}N{\cdot}NO_2 + H_2O$.

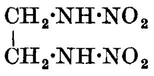
---

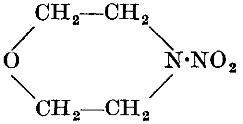
[1] M. I. Gillibrand and A. H. Lamberton, *J.*, 1949, 1883.
[2] *J. Org. Chem.*, 1947, **12**, 373.

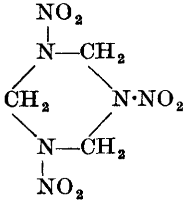
TABLE I

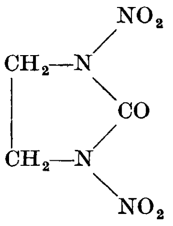
Type.	Typical examples.	Formula.	M.p.	B.p. (mm.).
Primary nitramines	Methylnitramine	I; R = H, R′ = Me	38°	
	Ethylenedinitramine	II	175	
	Phenylnitramine	I; R = H, R′ = Ph	46	
Secondary nitramines	Dimethylnitramine	I; R=R′=Me	58	187°/759
	4-Nitromorpholine	III	53	84°/1·3
	Cyclonite, or R.D.X. (1 : 3 : 5-trinitrohexahydro-1 : 3 : 5-triazine)	IV	205	
	Tetryl (2 : 4 : 6-trinitrophenylmethylnitramine)	I; R = Me, R′ = picryl	130	
Primary nitramides	Nitrourethane	I; R = H, R′ = CO_2Et	64	
	Nitrourea	I; R = H, R′ = $CO·NH_2$	158 (decomp.)	
Secondary nitramides	*N*-Nitro-*N*-carbomethoxymethylamine	I; R = Me, R′ = CO_2Me	8	93°/15
	Ethylenedinitrourea (1 : 3-dinitro-2-ketotetrahydroglyoxaline)	V	210	
	N-Nitro-*N*-benzyltoluene-*p*-sulphonamide	I; R=CH_2Ph, R′ = $SO_2·C_6H_4Me$	79	

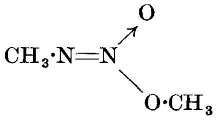

(I.)

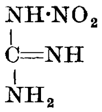

$$\begin{array}{l} CH_2·NH·NO_2 \\ | \\ CH_2·NH·NO_2 \end{array}$$
(II.)


(III.)


(IV.)


(V.)


(VI.)


$$\begin{array}{l} NH·NO_2 \\ | \\ C{=}NH \\ | \\ NH_2 \end{array}$$
(VII.)

A nitramine (or, more accurately, a mixture of primary nitramides) appears to have been isolated for the first time in 1869 by P. Griess.[3] The structure of tetryl, prepared in 1877 by K. H. Mertens [4] from dimethylaniline, was elucidated in 1883 by P. van Romburgh [5]; and other members

---

[3] *Ber.*, 1869, **2**, 434; 1872, **5**, 192; for structure see Th. Zincke, *Annalen*, 1896, **291**, 319.
[4] *Ber.*, 1877, **10**, 995.
[5] *Rec. Trav. chim.*, 1883, **2**, 103.

of the group, both aromatic and aliphatic, were soon produced. The major features of their chemistry were established in the years 1883—1914 ; the names of Romburgh, A. P. N. Franchimont, J. Thiele, A. Hantzsch, E. Bamberger, and K. J. P. Orton are prominent. An exhaustive review of this work (to 1912) has been given by H. J. Backer.[6] Between 1914 and 1939 developments in this field, apart from the investigation of the decomposition of nitramine (which will not be reviewed here), were slight. On account of the increasing importance of nitramines as explosives, a considerable programme of research has been carried out during the past ten years. It is to be regretted that much material of scientific value remains unpublished ; and this review must inevitably appear unbalanced to those acquainted with all the recent investigations. The use of tetryl as an intermediate, or " booster ", between the detonator and the main charge of shells or bombs is well known. Cyclonite, which may be handled as a slurry in T.N.T., has been employed in mixtures designed to give a maximum of brisance ; and, with suitable additions, can be obtained as a putty-like " plastic explosive " (" P.E.") for use in hurried demolitions. Nitroguanidine (VII) has found application as a constituent of flashless propellants.

Preparation and Properties

Since *N*-nitro-compounds do not figure prominently in many textbooks, a brief review of the main features of their chemistry may be of value. They do not show any trace of basic properties—at least in the ordinary meaning of the term—and the primary compounds are markedly acidic : the compound $R{\cdot}NH{\cdot}NO_2$ is normally about one-twentieth as strong as $R{\cdot}CO_2H$, and nitrourethane is stronger than formic acid. Some nuclear-nitrated arylnitramines are yellow, but are paler than the corresponding nitroanilines. With these exceptions, all are colourless. Ultra-violet absorption spectra have been measured.[7]

In spite of the outstanding explosive properties of some members, the group $>\!N{\cdot}NO_2$ cannot be considered to be inherently unstable in a manner comparable with, say, diazonium salts or azides. Many nitramines decompose explosively when heated ; but, on the other hand, distillation of aliphatic secondary nitramines and of *N*-alkylnitrourethanes seems to be generally practicable under reduced pressure.

Methods of Preparation.—Nitramides may be prepared by direct nitration of amides. Only a few primary nitramides are known, and their rarity may be due to the decomposition of many, which might otherwise be isolable, under the conditions of nitration. Direct conversion of the monoalkylated amides, $R{\cdot}CO{\cdot}NHR'$, into the secondary nitramides, $R{\cdot}CO{\cdot}N(NO_2)R'$, is, as a rule, readily effected by absolute (100%) nitric acid alone.* Mixtures of nitric acid with sulphuric acid or acetic anhydride have also been

---

[6] *Ahrens Sammlung*, 1912, **18**, 359.

[7] E. C. C. Baly and C. H. Desch, *J.*, 1908, **93**, 1747 ; M. Carmack and J. J. Leavitt, *J. Amer. Chem. Soc.*, 1949, **71**, 1221 ; see also ref. 43.

* Acid containing *ca.* 98% by weight of HNO_3 is often used in practice.

employed ; it seems that the use of the anhydride is often advantageous, but it may be doubted whether sulphuric acid exercises a favourable influence comparable with that shown in aromatic nitration.

Aliphatic primary nitramines are rapidly decomposed by concentrated acids, and cannot be prepared by direct nitration of the corresponding amine. The commonest preparative route is through acylation of the amine, nitration to the secondary nitramide, and decomposition of the latter (which often need not be purified) by means of alkalis to yield the salt of the required nitramine. Urethanes have been widely used as the intermediate nitratable amides, but acetyl and oxalyl derivatives have also been employed. The secondary nitramides seem, in general, to be sufficiently stable to allow their ethereal solutions to be freed from nitric acid by washing with cold aqueous sodium hydrogen carbonate, but are decomposed readily enough by warming with aqueous ammonia or sodium hydroxide : in some cases [especially cyclic nitramides : *e.g.*, (V) ⟶ (II) [8, 9]] boiling with water suffices. With the urethanes a particularly convenient technique may be employed. On treatment of an ethereal solution of the crude alkylnitrourethane with gaseous ammonia (or an aliphatic amine) the salt of the nitramine is precipitated, and the carbethoxyl group is converted into the ether-soluble urethane. Thus methylnitramine (VIII) can conveniently be prepared by route (A) :

$$\begin{tikzcd}
\text{(A)}\quad \text{Me}\cdot\text{NH}_2 \arrow[r, "\text{Cl}\cdot\text{CO}_2\text{Et}"] & \text{Me}\cdot\text{NH}\cdot\text{CO}_2\text{Et} \arrow[r, "\text{HNO}_3\,[10]"] & \text{Me}\cdot\text{N(NO}_2)\cdot\text{CO}_2\text{Et} \arrow[d, "2\text{NH}_3"] \\
 & \underset{\text{(VIII.)}}{\text{Me}\cdot\text{NH}\cdot\text{NO}_2} & \text{Me}\cdot\underbrace{\text{N}\cdot\text{NO}_2}_{\text{NH}_4}\ (+\,\text{NH}_2\cdot\text{CO}_2\text{Et}) \arrow[l, "\text{Acid}"']
\end{tikzcd}$$

The nitramines are obtained from their salts by acidification, and collection or ether extraction : care is necessary, since warming with mineral acids leads to rapid decomposition.

Until Wright's recent discovery that secondary aliphatic amines could be satisfactorily nitrated in the presence of a catalyst (p. 82), the corresponding nitramines have normally been obtained by the nitrolysis of suitable dialkylamides in accordance with scheme (B). In nitrolysis,* as opposed to nitration, rupture of a nitrogen–carbon bond takes place ; and, alternatively, a secondary nitramide may be formed [equation (C)] :

$$\begin{tikzcd}
\text{X}\cdot\text{CO}\cdot\text{NR}_2 + \text{HO}\cdot\text{NO}_2 \arrow[r, "\text{(B)}"] \arrow[dr, "\text{(C)}"'] & \text{X}\cdot\text{CO}_2\text{H} + \text{R}_2\text{N}\cdot\text{NO}_2 \\
 & \text{X}\cdot\text{CO}\cdot\text{N(NO}_2)\cdot\text{R} + \text{R}\cdot\text{OH}
\end{tikzcd}$$

---

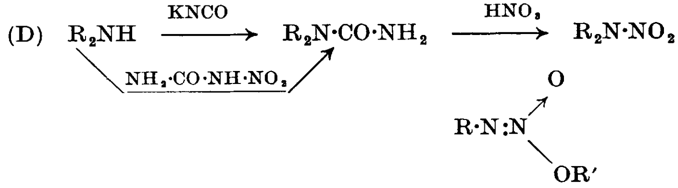
[8] A. P. N. Franchimont and E. A. Klobbie, *Rec. Trav. chim.*, 1888, **7**, 17.

[9] W. E. Bachmann *et al.*, personal communications.

[10] The nitration of Me·NH·CO$_2$Et does not appear to be reported in Beilstein, though it proceeds smoothly (A. P. N. Franchimont, *Rec. Trav. chim.*, 1894, **13**, 308).

* A term first introduced by R. P. Linstead (personal communication).

Franchimont[11] accumulated much information regarding the influence of the group X on the course of the reaction. Route (D) has been commonly employed : an interesting alternative method of producing the intermediate dialkylurea is by the use of nitrourea, which decomposes in aqueous solution to act as a source of cyanic acid.[12]



$$\begin{tikzcd}
\text{(D)}\ R_2NH \arrow[r, "KNCO"] \arrow[r, bend right, "NH_2{\cdot}CO{\cdot}NH{\cdot}NO_2"'] & R_2N{\cdot}CO{\cdot}NH_2 \arrow[r, "HNO_3"] & R_2N{\cdot}NO_2
\end{tikzcd}$$

(IX.)

It is also possible to produce secondary nitramines by treatment of the potassium or silver salts of the primary compounds with an alcoholic solution of an alkyl halide. Mixtures commonly result,[13, 14] and the method is not of much practical value save for the preparation of the *O*-alkyl isomers (IX). Diazomethane converts methylnitramine quantitatively into dimethylnitramine, but with phenylnitramine the *O*-alkyl compound (IX ; $R = Ph$, $R' = Me$) is the main product.[15]

The methods of preparation which have been mentioned cannot (with some few exceptions) be applied in the aromatic series. The direct nitration of suitable (usually weakly basic) anilines can be effected by the successive addition of anhydrous nitric acid and acetic anhydride to a suspension of the aniline in acetic acid,[16] or by " dehydration " of the solid base nitrate by adding it to acetic anhydride.[17] Aryl primary nitramines without nuclear nitro-groups (*e.g.*, phenylnitramine) are best prepared by oxidation of diazoates : $Ph{\cdot}N{:}NOK \xrightarrow{O} Ph{\cdot}NK{\cdot}NO_2$. Alkaline ferricyanide is a convenient reagent.[18]

Action of Acids and Alkalis.—Refluxing with dilute (2%) aqueous sulphuric acid converts aliphatic primary nitramines into alcohols, with quantitative production of nitrous oxide :[6, 19] $R{\cdot}NH{\cdot}NO_2 \rightarrow R{\cdot}OH + N_2O$. Concentrated mineral acids bring about a similar decomposition rapidly : thus methylnitramine is attacked by absolute nitric acid, even below 0°, to yield nitrous oxide and methyl nitrate.[20] Acidic reagents promote rearrangement of aromatic nitramines (primary or secondary) to the isomeric

---

[11] *Rec. Trav. chim.*, 1883, **2**, 121 ; and numerous papers in the same journal to 1909 : see ref. 6, pp. 376—378.

[12] T. L. Davis and K. C. Blanchard, *J. Amer. Chem. Soc.*, 1929, **51**, 1790.

[13] E. Bamberger, *Ber.*, 1894, **27**, 359.

[14] H. Umbgrove and A. P. N. Franchimont, *Rec. Trav. chim.*, 1898, **17**, 270.

[15] O. Degner and H. von Pechmann, *Ber.*, 1897, **30**, 646.

[16] K. J. P. Orton, *J.*, 1902, **81**, 806 : E. Macciotta, *Chem. Abs.*, 1942, **36**, 1593. For other (early) references see ref. 6.

[17] E. Hoff, *Annalen*, 1900, **311**, 99.

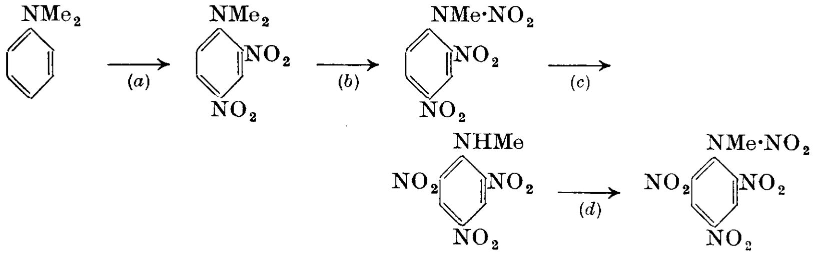
[18] J. Houben, " Die Methoden der Organischen Chemie ", 3rd Edn., 1941, **4**, 262.

[19] H. van Erp, *Rec. Trav. chim.*, 1895, **14**, p. 40 *et seq.*

[20] A. P. N. Franchimont, *ibid.*, 1910, **29**, 296.

C-nitroanilines.[21, 22, 23] Recent research has shown that this rearrangement is of importance in the preparation of tetryl. As shown in route (E), the combined nitration and nitrolysis of dimethylaniline (by nitric and sulphuric acid) probably involves (*a*) dinitration of the benzene ring, (*b*) nitrolysis to the nitramine, (*c*) intramolecular change to *N*-methylpicramide, and (*d*) the final nitration to tetryl.[24]

(E)



In contrast with primary nitramines, the secondary compounds may be prepared in the presence of absolute nitric acid, often resist the action of 40% aqueous sulphuric acid at 100°, and are unaffected by the latter reagent at room temperature.[25] Such behaviour differentiates them from their *O*-alkyl isomers, which decompose smoothly in the cold: [26]

$$R\cdot N{:}NO\cdot OR' + H_2O \xrightarrow[H_2SO_4]{40\%} R\cdot OH + N_2O + R'\cdot OH$$

Most—but by no means all—primary nitramines show a high degree of stability towards alkalis, and, apart from being converted into their salts, are not attacked by 10—20% aqueous sodium hydroxide at 100°.[19] Secondary aliphatic nitramines are decomposed with varying ease by heating with aqueous sodium hydroxide. The overall decomposition is said to follow the course $R\cdot N(NO_2)\cdot CH_2R' \xrightarrow{-HNO_2} R\cdot N{:}CHR' \rightarrow R\cdot NH_2 + R'\cdot CHO$,[19, 27] and the production of nitrous acid may be made the basis of a sensitive colorimetric test.[28]

Action of Reducing Agents.—Vigorous reduction ruptures the N–N linkage to yield amines and ammonia. Milder conditions give rise to a wide variety of products, usually in very poor yield: the early work has been summarised

---

[21] E. Bamberger and K. Landsteiner, *Ber.*, 1893, **26**, 490.

[22] A. E. Bradfield and K. J. P. Orton, *J.*, 1929, 915.

[23] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry", 1949, pp. 225—229; E. D. Hughes and G. T. Jones, *J.*, 1950, 2678.

[24] C. E. Clarkson, I. G. Holden, and T. Malkin, *J.*, 1950, 1556. For suggested routes under a variety of conditions see E. D. Hughes, C. K. Ingold, *et al.*, *J.*, 1950, 2657.

[25] A. P. N. Franchimont and H. Umbgrove, *Rec. Trav. chim.*, 1898, **17**, 287.

[26] Ref. 25, and personal communications; also W. R. Kingdom and G. F. Wright, *J. Amer. Chem. Soc.*, 1950, **72**, 1030.

[27] A. P. N. Franchimont and H. van Erp, *Rec. Trav. chim.*, 1895, **14**, 224.

[28] R. L. Shriner, personal communications.

in detail by H. J. Backer [29] and, apart from the reduction of nitroguanidine,[30] little attention has been recently given to this field. The so-called " diazotisation " of primary aromatic nitramines [31] is formally a reduction, and possibly proceeds by way of nitrosation : [32]

$$\begin{array}{l} Ar{\cdot}NH{\cdot}NO_2 + HNO_2 \longrightarrow Ar{\cdot}N(NO){\cdot}NO_2 + H_2O \longrightarrow Ar{\cdot}NH{\cdot}NO + HNO_3 \\ \hspace{22em}\downarrow \\ \hspace{19em}[ArN_2]^+ \overset{-}{NO_3} + H_2O \end{array}$$

Novel Methods of Preparation

Primary Nitramines.—It has long been known that methylnitramine could be prepared from nitrourethane—which is readily obtainable by direct nitration [33]—through alkylation and subsequent ammonolysis.[34] It has now been shown that, if substituted diazomethanes are employed to effect the alkylation, otherwise inaccessible nitramines, containing easily nitratable benzene rings, can be produced ;[1] and the preparation of benzhydrylnitramine (X) serves as an example :

$$Ph_2CO \xrightarrow{NH_2{\cdot}NH_2} Ph_2C{:}N{\cdot}NH_2 \xrightarrow{HgO} Ph_2CN_2 \xrightarrow{NH(NO_2){\cdot}CO_2Et}$$

$$Ph_2CH{\cdot}N(NO_2){\cdot}CO_2Et \xrightarrow[\text{acidification}]{\text{ammonolysis and}} Ph_2CH{\cdot}NH{\cdot}NO_2 \quad (X.)$$

A completely new route (F) to primary nitramines has been found by G. N. R. Smart and G. F. Wright.[35] When *NN*-dichloroamines in an excess of acetic anhydride are treated with a molecular proportion of 99% nitric acid, chlorine is evolved, and evaporation *in vacuo* yields a residue of crude *N*-chloronitramine. The halogen in compounds of this type is positive in character, and can be removed by reducing agents, such as aqueous sodium thiosulphate, to yield the primary nitramine.

$$(F) \quad R{\cdot}NCl_2 \xrightarrow{HNO_3\ \&\ Ac_2O} R{\cdot}N(NO_2)Cl \xrightarrow{Na_2S_2O_3} R{\cdot}NH{\cdot}NO_2$$

Secondary Nitramines.—E. Bamberger and A. Kipal [36] obtained small yields of dimethylnitramine and of nitropiperidine by " dehydration " of the base nitrate with acetic anhydride. Wright and his co-workers have investigated this reaction in detail. When diethanolamine was treated with an excess of nitric acid, the hydroxyl groups were esterified and 2 : 2′-dinitroxydiethylammonium nitrate could be isolated. This, after drying in a desiccator over calcium chloride, could be converted in good yield

---

[29] Ref. 6, pp. 408—412 ; *Rec. Trav. chim.*, 1912, **31**, 1, 142.

[30] G. B. L. Smith *et al.*, papers in *J. Amer. Chem. Soc.*, 1932 to 1937 ; E. Lieber and G. B. L. Smith, *Chem. Reviews*, 1939, **25**, 213.

[31] E. Bamberger, *Ber.*, 1897, **30**, 1248.

[32] T. S. Stevens, personal communication.

[33] R. C. Brian and A. H. Lamberton, *J.*, 1949, 1633.

[34] J. Thiele and A. Lachman, *Annalen*, 1895, **288**, 291 ; J. L. Heinke, *Ber.*, 1898, **31**, 1935.

[35] *Canad. J. Res.*, 1948, **26**, *B*, 284.

[36] *Ber.*, 1895, **28**, 535.

by acetic anhydride into 2 : 2′-dinitroxydiethylnitramine [" DINA "; $NO_2{\cdot}N(CH_2{\cdot}CH_2{\cdot}O{\cdot}NO_2)_2$,][37] but the yield was unsatisfactory after drying the salt in a current of air. In the desiccator some interchange of nitrate and chloride had occurred between the ammonium salt and the desiccant; and it was thus discovered that chlorides were catalysts for this nitration of aliphatic amines. It was found possible to dispense with the isolation of the intermediate nitrate. A small quantity of diethanolamine hydrochloride was used as a catalyst; the main bulk of diethanolamine and the nitric acid were added dropwise and simultaneously to the acetic anhydride. Yields of 90% were obtained.[37]

The technique of catalytic nitration has also been applied to other secondary amines, by treatment, in general, of the amine nitrate with acetic anhydride containing zinc chloride. The conversion into the corresponding nitramine of the nitrates of dimethylamine, diethylamine, piperidine, and morpholine has been achieved in, respectively, 65, 60, 58, and 65% yields; and the hydrochloride of di-*n*-butylamine has been converted into the nitramine in 65% yield by reaction, for 24 hours at 20°, with just over two molecular proportions of nitric acid and of acetic anhydride.[37, 38]

Wright has shown [38, 39] that the nitration of $\rangle NH$ to $\rangle N{\cdot}NO_2$ is dependent upon the basicity of the imino-group. This, in general terms, was already known: Franchimont's rule [40] for the nitration of cyclic amides states that $\rangle NH$ is not substituted by nitric acid if present as an imide or an amine (*e.g.*, ·CO·NH·CO· or $\cdot CH_2{\cdot}NH{\cdot}CH_2\cdot$), whilst amides (*e.g.*, $\cdot CH_2{\cdot}NH{\cdot}CO\cdot$) are nitrated. Nitration of the diacylamine still awaits accomplishment, but some secondary amines have been nitrated in reasonable yield even without catalytic assistance.[40, 41] Such compounds [*e.g.*, $R{\cdot}CH_2{\cdot}NH{\cdot}CH_2R$, where R = CN, CO_2H, or $CO{\cdot}NH_2$; and $NH(CHMe{\cdot}CN)_2$] are weak bases, and the proton-attractive capacity of the imino-group is approximating towards that exhibited by normal amides.

In the recent Canadian work [39] the basicity of a series of secondary amines in acetic acid solution has been examined by colorimetric methods,[42] *o*-nitroaniline being used as indicator, and sulphuric or perchloric as strong acid. These results have been compared with the ease of nitration.[38] It has been found that amines which are nitrated in good yield without the necessity of a catalyst are considerably weaker than morpholine, whilst for strong amines (*e.g.*, di-*n*-butylamine) the " catalyst " is best employed in an equimolar proportion. It was concluded [39] that (1) since strongly basic

---

[37] W. J. Chute, K. G. Herring, L. E. Toombs, and G. F. Wright, *Canad, J. Res.*, 1948, **26**, *B*, 89.

[38] W. J. Chute, G. E. Dunn, J. C. MacKenzie, G. S. Myers, G. N. R. Smart, J. W. Suggitt, and G. F. Wright, *ibid.*, p. 114.

[39] G. E. Dunn, J. C. MacKenzie, and G. F. Wright, *ibid.*, p. 104.

[40] A. P. N. Franchimont and J. V. Dubsky, *Rec. Trav. chim.*, 1916, **36**, 80.

[41] J. V. Dubsky, *Ber.*, 1916, **49**, 1045.

[42] N. R. Hall *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 2487, 2493.

amines are not attacked in the absence of a catalyst,* nitration does not take place through the normal electrovalent ammonium salt ; (2) since the diacylamines are resistant, the capacity to form a " salt " of some kind is essential ; and (3) the catalyst must act to decrease, in some manner the effective basicity of the amine.

The nature of the catalytic action was investigated in a series of papers.[38, 43–46] It was found that electropositive chlorine existed in the reaction mixtures, and that this, probably in the form of chlorine acetate, attained a sufficient concentration to convert the secondary amine into the less basic chloramine. The action on dialkylchloramines of nitric acid-acetic anhydride mixtures, or of nitric acid alone, was examined ; and in most, though not all, cases a satisfactory conversion into the nitramine was achieved. Since electropositive chlorine was regenerated, the catalysed nitration of the parent amines can be considered as a self-sustaining chain reaction. Examination of the by-products resulting from the nitration of chloramines apparently indicated that chloramine nitration, and not chloramine formation, was the rate-determining step in the catalysed reaction.

Mechanism of Nitration and Nitrolysis

Wright suggests [39, 44] that the nitration of secondary amines (and presumably also of amides) proceeds through the formation of a nitrogen–nitrogen bonded complex of the amine and nitric acid. The nitric acid is pictured as reacting, in the form (XI), with the lone pair of the imino-nitrogen to yield the " salt " (XII). It is held that such complexes are not formed by the non-basic diacylamines, or by the strongly basic amines, which yield the normal electrovalent salts. The nitramine is then formed by elimination of X•OH from the complex, X being equivalent to Cl in catalysed, and to H in uncatalysed nitrations. The complex may be considered, if desired, in the ionic form (XIII) : loss of X^+ yields the nitramine. (*See scheme on next page.*)

In this mechanism of nitration no mention is made of the nitronium ion. The distinction involved is perhaps more apparent than real. Union of the free base with the nitronium $(NO_2)^+$ ion would yield, directly, the cation of the electrovalent form (XIII) of Wright's complex. It may be that amine (and amide) nitration is best considered as the result of two competing reversible bimolecular reactions (G, H), followed, in one case, by the ejection of a hydrogen ion.† Such a mechanism differs from that postulated for aromatic nitration in (1) the existence of a competing reaction

[43] J. C. MacKenzie, G. S. Myers, G. N. R. Smart, and G. F. Wright, *Canad, J. Res.*, 1948, **26**, *B*, 138.

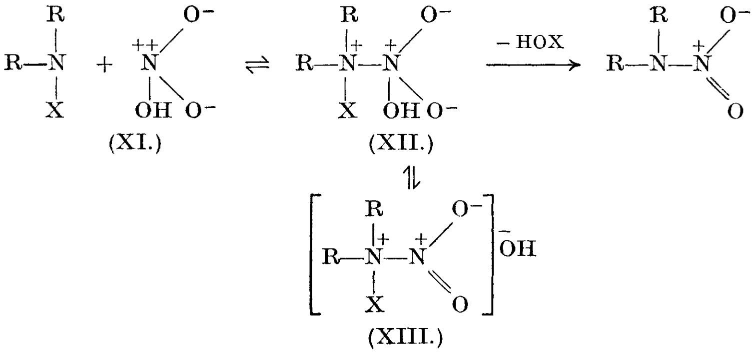
[44] G. S. Myers and G. F. Wright, *ibid.*, p. 257.

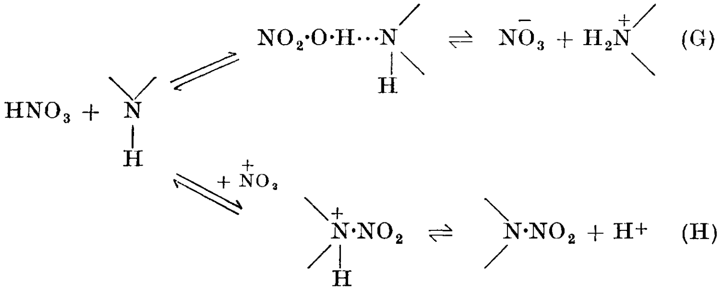
[45] K. K. Carroll and G. F. Wright, *ibid.*, p. 271.

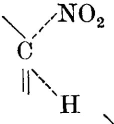
[46] T. Connor, G. N. R. Smart, and G. F. Wright, *ibid.*, p. 294.

* Small quantities of the nitramine may be obtained : thus prolonged treatment of the nitrates of dimethylamine and piperidine with acetic anhydride gave the corresponding nitramines, in, respectively, 5 and 22% yield.

† The basicity of the $>N{\cdot}NO_2$ group has never been demonstrated. It certainly does not accept a proton readily.





(G), and (2) the comparative stability which might be attributed to $>\overset{+}{N}H{\cdot}NO_2$ in contrast with the transition state  * Strong bases may be converted almost wholly into the quaternary $>\overset{+}{N}H_2$ form, and bases weaker than amides may not react with the nitronium ion : in neither case will nitramine formation occur. Experimental evidence for the reversibility of the nitration process is furnished by nitrourethane [47] and by *N*-methylnitrourethane,[48] both of which can act as nitrating agents in a sulphuric acid medium. Again, many aromatic nitramines, as discovered by Romburgh,[49] can be de-nitrated to the amine by heating with phenol and, usually, a little sulphuric acid ; [6] but it must be noted that the treatment of secondary aliphatic nitramines with concentrated sulphuric acid does not appear, at least on the scanty evidence which exists,[6, 25] to give rise to nitric acid.

Such competing equilibria might also be applied to the process of nitrolysis, and this would allow the two modes of action of nitric acid to be unified from the mechanistic point of view. Nitrolysis has generally been considered as involving nitramine and alcohol formation, followed by

---

[47] J. Thiele, *Annalen*, 1897, **296**, 108.

[48] A. H. Lamberton, unpublished data.

[49] *Rec. Trav. chim.*, 1886, **5**, 240.

* *Added in Proof.*—Or in contrast with the intermediate compound $Ar^{+}H(NO_2)$, suggested by E. D. Hughes, C. K. Ingold, and R. I. Reed, *J.*, 1950, 2400.

esterification (J). It may well be, however, that the alcohol is never produced, and that nitrolysis proceeds by the route (K).

$$\begin{tikzcd}[column sep=small] \text{(J)}\quad R_2N{\cdot}CH_2R' + HO{\cdot}NO_2 \arrow[r] & R_2N{\cdot}NO_2 + HO{\cdot}CH_2R' \arrow[r, "HNO_3"] & NO_2{\cdot}O{\cdot}CH_2R' \\ & & & + \overset{-}{NO_2} \arrow[ul] \end{tikzcd}$$

$$\text{(K)}\quad R_2N{\cdot}CH_2R' + NO_2{}^{+} \rightarrow R_2\overset{+}{N}(NO_2){\cdot}CH_2R' \rightarrow R_2N{\cdot}NO_2 + \overset{+}{C}H_2R'$$

It must be made clear that these suggestions are speculative, and it is perhaps over-optimistic to hope that they will be generally applicable.

Structure and Tautomerism

Representative members of all classes of nitramines have been reduced to hydrazine derivatives, and the yields obtained from some groups, such as the secondary nitramines, are good.[29] Though the yields from the other classes may be poor, the inter-relationship of the various substances shows with almost complete certainty the presence of a nitrogen–nitrogen linkage in the nitramines and nitramides. The comparative stability of the primary nitramines to alkali excludes a nitrite (R·NH·O·NO) structure, and further proof of the universality of the N–N linkage is given by the preparation of aromatic primary nitramines by the oxidation of diazoates. *X*-Ray analyses of ethylenedinitramine and dimethylnitramine provide conclusive support for the chemical evidence.

The essential difference between the nitramines and the nitrosohydroxylamines (which, also, have given small yields of hydrazines on reduction) lies in the disposition of the oxygen atoms. The extensive use of simple nitrating agents in the preparation of nitramines and nitramides suggests the attachment of both oxygen atoms to the same nitrogen, while in the preparation of nitrosohydroxylamines nitrosating agents are employed. There is convincing evidence that the nitrosohydroxylamines are neither identical nor tautomeric with the isomeric nitramines [*e.g.*, phenylnitrosohydroxylamine, Ph·N(NO)·OH, the acid of cupferron ; and phenylnitramine, Ph·NH·NO$_2$]. Aliphatic nitrosohydroxylamines are in general only isolable as salts, but the isomeric pair

$$(CH_2{\cdot}OH)_3C{\cdot}N(NO){\cdot}OH \quad \text{and} \quad (CH_2{\cdot}OH)_3C{\cdot}NH{\cdot}NO_2$$

has recently been synthesised.[50]

Primary Nitramines.—Hantzsch [51] formulated primary nitramines as pseudo-acids ($R{\cdot}NH{\cdot}NO_2 \rightleftharpoons R{\cdot}N{:}NO{\cdot}OH$) on the grounds of delayed precipitation of their ammonium salts in benzene, and the large temperature coefficient of their conductivities. This view has persisted [52] though it rests on little save Hantzsch's prestige and the formal analogy with the nitroparaffins. H. Euler,[53] in a vigorous attack, showed that the observations with regard to the ammonium salts were incorrect—a fact admitted by

---

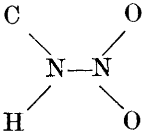
[50] J. Cason and F. S. Prout, *J. Amer. Chem. Soc.*, 1949, **71,** 1218.

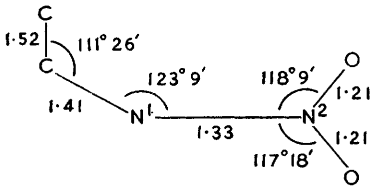
[51] A. Hantzsch and F. E. Dollfus, *Ber.*, 1902, **35,** 258.

[52] N. V. Sidgwick, T. W. J. Taylor, and W. Baker, " The Organic Chemistry of Nitrogen ", 1937, p. 454.

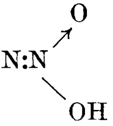
[53] *Ber.*, 1906, **39,** 1607.

Hantzsch [54]—and claimed that the conductivity results were not abnormal. Indeed, since the dissociation constants of carboxylic acids show a maximum value at about room temperature, and weaker acids do not reach their maximum until a higher temperature is attained, the nitramino-acids might be expected to show a somewhat higher temperature coefficient of dissociation—over, say, the range 0—25°—than their carboxylic analogues. Again, though primary nitramines react with formaldehyde and bases in a manner formally analogous to the nitroparaffins, recent research has shown that the chemical nature of the products is markedly different (p. **93**); and methylmagnesium iodide reacts with an excess of methylnitramine to give, in contrast with the nitroparaffins,[55] an immediate evolution of gas.[48] Only in one case [56] does the literature contain any suggestion that normal and *aci*-forms have a real existence. R. P. Bell [57] suggests that the term pseudo-acid should be reserved "for molecules in which there are strong experimental or theoretical reasons for believing that the charge on the ion is concentrated chiefly on atoms other than that from which the proton has been removed". It does not appear that primary nitramines (or nitramides) fulfil this requirement.

The structure of ethylenedinitramine has been determined through *X*-ray analysis by F. J. Llewellyn and F. E. Whitmore.[58] In agreement with the earlier work of W. Costain and E. G. Cox [59] on dimethylnitramine, the group  was found to be planar; the final structure deduced is (XIV), where distances are given in A. The nitro-group appears normal, the valency angles being close to those observed in *p*-dinitrobenzene, and the N^2–O



(XIV.) (NOT TO SCALE)

separation, though slightly smaller than that found (1·23 A.) in *p*-dinitrobenzene, agrees with the value found in nitromethane: by implication the un-ionised nitramino-structure is $\cdot NH\cdot NO_2$, rather than  $\cdot N{:}N\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}$. There

---

[54] *Ber.*, 1907, **40**, 3804.

[55] G. D. Buckley, *J.*, 1947, 1492.

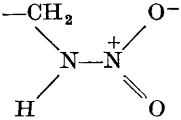
[56] K. J. P. Orton, *J.*, 1902, **81**, 965.

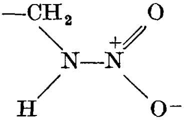
[57] *Quart. Reviews*, 1947, **1**, 121.

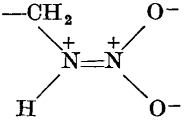
[58] *J.*, 1948, 1316.

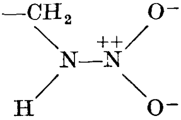
[59] *Nature*, 1947, **160**, 826.

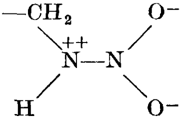
is nevertheless considerable shortening of the C–N[1] and the N[1]–N[2] bonds in comparison with the sums of the covalent radii (1·41 and 1 33, compared with 1·47 and 1·40 A., respectively). In the case of the first bond the conclusion was drawn that there is an electronic drift from N[1], leaving a positive charge which reduces the nitrogen single-bond radius : the value is identical with that found for C–N in *p*-dinitrobenzene. The short N[1]–N[2] bond may indicate that this has about 15% double-bond character, and the canonical forms (XV), (XVI), and (XVII) contribute to the resonance structure of the molecule, the contribution of (XVII) maintaining the carbon, nitrogen, and oxygen atoms in one plane. On the ground that structure (XVII) invalidates Pauling's adjacent-charge rule, Llewellyn and Whitmore preferred to replace it by (XVIII) and (XIX) ; it is not, however, clear to the Reviewer in what respect the sum of these contributions would really differ from a contribution by (XVII), and it might seem better to specify the hybrid structure, rather loosely, as (XX).

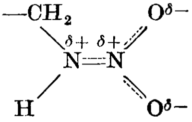

(XV.)


(XVI.)

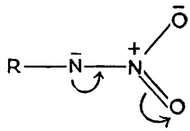

(XVII.)


(XVIII.)

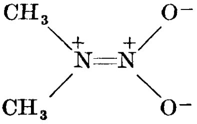

(XIX.)


(XX.)

In addition, hydrogen bonding presumably occurs between N[1] and the oxygen of an independent nitramino-group. The structural forms ·NH·NO$_2$ and ·N:NO·OH can be regarded, in L. Hunter's nomenclature,[60] as a pair of mesohydric tautomers. In their salts the anions clearly have the mesomeric structure shown inset.



Secondary Nitramines.—The general structure RR′N·NO$_2$ is suggested by the formation of good yields of *as*-dialkylhydrazines on reduction, and the equivalent positions of the alkyl (or aryl) groups can be demonstrated by convergent syntheses (*e.g.*, methylethylnitramine can be produced by methylation of ethylnitramine or by ethylation of methylnitramine). Costain and Cox [59] attribute the planarity of the dimethylnitramine molecule to a contribution by the canonical form (XXI).


(XXI.)

***O*-Alkyl Derivatives of Primary Nitramines.**—These are produced at the same time, and by the same processes of alkylation, as the isomeric secondary nitramines. The structure R·N:NO·OR′ appears reasonable, and is sup-

---

[60] *J.*, 1945, 806.

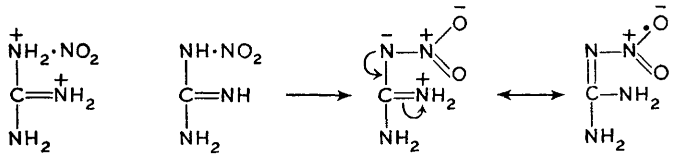
ported by the rupture of these compounds with 40% sulphuric acid to yield the alcohols R·OH and R′·OH.

Primary Nitramides.—The structure of this small group rests on their production (when decomposition does not occur) by the direct nitration of amides, and on their reduction in good yield to hydrazides. In their reactions as acids they are presumably completely analogous to the primary nitramines.

Secondary Nitramides.—Only one member [$Me{\cdot}N(NO_2){\cdot}CO_2Et$] has been reduced to the corresponding hydrazide.[29] The structure of these compounds rests mainly on their production by direct nitration of substituted amides and is confirmed both by convergent syntheses and by hydrolysis to primary nitramines.

Nitroguanidine

According to Wright's investigation (p. 82), strong bases are not nitrated readily, and it may be suggested that the facile formation of nitroguanidine (XXII) from guanidine nitrate and sulphuric acid [61] is essentially a conversion of the (weakly basic ?) guanidine cation into the nitroguanidine cation through the doubly charged (XXIII).* The nitration of *N*-alkylguanidines on the N′ atom [62] is consonant with this opinion. Nitroguanidine is an extremely weak acid and base, comparable in strength with, respectively, phenol and urea; and it does not behave chemically as a primary nitramine. Its zwitterionic nature (m.p. *ca.* 230°, decomp.; more soluble in water than in organic solvents) is generally recognised.[63] Such a structure (XXIV), obtained from (XXII) by proton transfer, may exhibit both nitramino- and amidine resonance; and the C–NH$_2$, N–N, and N–O bonds are all probably of fractional order. Also, in contrast with zwitterionic amino-acids, there seems to be no impediment to the indicated electron shift, which could yield the covalent (XXV). According to Wright,[64] this " nitrimino "-structure is worthy of serious consideration. It thus appears that, in theory, no one bond in the molecule is uniquely



(XXIII.) (XXII.) (XXIV.) (XXV.)

[61] T. L. Davis, *Org. Synth.*, 1927, **7**, 68.

[62] T. L. Davis and R. C. Elderfield, *J. Amer. Chem. Soc.*, 1933, **55**, 731.

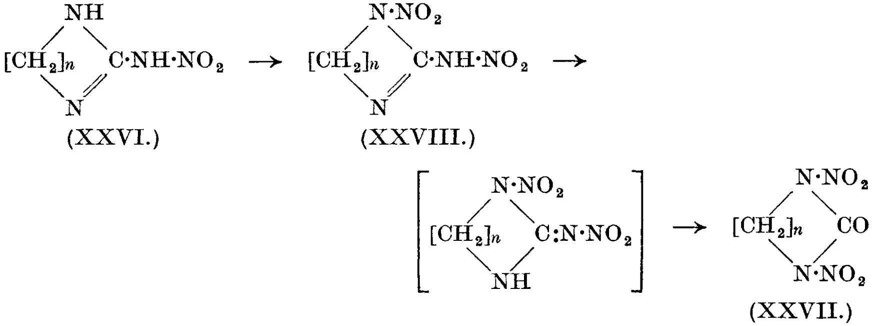
[63] C. Hahn, E. Pribyl, E. Lieber, B. P. Caldwell, and G. B. L. Smith, *ibid.*, 1944, **66**, 1223.

[64] G. F. Wright, personal communication.

* The kinetics of the reaction are under investigation by G. Williams and R. J. J. Simkins (personal communication).

single or double : an *X*-ray examination would be of interest. Crystalline forms have been investigated.[65]

From nitroguanidine a wide variety of *N'*-alkyl or -aryl derivatives [$R{\cdot}NH{\cdot}C(NH){\cdot}NH{\cdot}NO_2$] have been produced by various routes.[66, 67] On treatment of nitroguanidine with aliphatic diamines, two molecules of ammonia are eliminated to give products which have been formulated as (XXVI ; $n = 2$, 3, and 4).[68] These are converted by an excess of nitric acid in acetic anhydride into the cyclic nitramides (XXVII).[69] The route shown has been suggested, and (XXVIII ; $n = 2$), which is formally a derivative of the unknown *NN'*-dinitroguanidine, has been isolated by the use of one molecular proportion of nitric acid. Treatment of (XXVI) with primary aliphatic amines effects replacement of $\cdot NH{\cdot}NO_2$ by $\cdot NHR$.[70]


(XXVI.) (XXVIII.) (XXVII.)

Methylenedinitramine, and the Dinitramine Series

When hexamine is added to nitric acid at — 40°, a solution is obtained from which the salt (XXIX) can be precipitated by ice [71] or by cautious dilution with water.[72] This nitrate is unstable in alkaline solutions ; and workers at Bristol University [72] thus isolated methylenedinitramine (XXX), in the form of its insoluble barium salt, by the use of barium hydroxide. Its preparation in good yield (25% w/w on acetamide) by a normal nitramine synthesis (L) has provided adequate proof of structure.[33] The nitration of a bisamide, incidentally, appears to be unusual ; nitrolysis is the commoner reaction. Thus attempts to make carbon-substituted methylenedinitramines were unsuccessful, and methylenediurethane (XXXI ; CO_2Et for each COMe) yielded nitrourethane.[33]

---

[65] T. L. Davis, A. A. Ashdown, and H. R. Couch, *J. Amer. Chem. Soc.*, 1925, **47,** 1063.

[66] T. L. Davis and S. B. Luce, *ibid.*, 1927, **49,** 2303.

[67] A. F. McKay, *ibid.*, 1949, **71,** 1968 ; also A. F. McKay and J. E. Milks, *ibid.*, 1950, **72,** 1616.

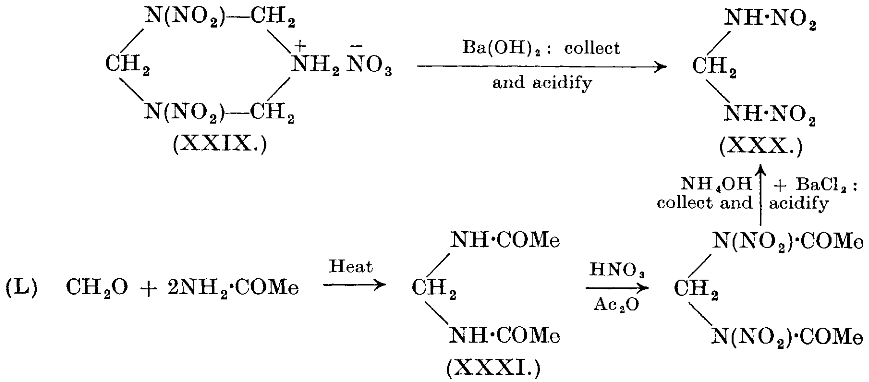
[68] A. F. McKay and G. F. Wright, *ibid.*, 1948, **70,** 430.

[69] *Idem, ibid.*, p. 3990 : A. F. McKay and D. F. Manchester, *ibid.*, 1949, **71,** 1970.

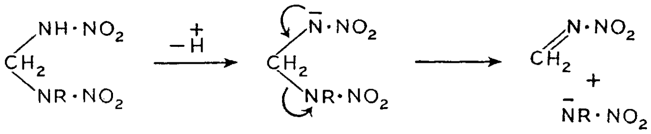
[70] A. F. McKay, M. N. Buchanan, and G. A. Grant, *ibid.*, p. 766.

[71] A. Vroom and C. Winkler, personal communication.

[72] E. L. Hirst, A. Carruthers, W. J. Dunning, J. K. N. Jones, H. D. Springall, *et al.*, personal communications,



Methylenedinitramine decomposes in strong mineral acids (10N. or upwards) and also in strong alkali (*e.g.*, 2N-sodium hydroxide). Around pH 1 or pH 10 the stability is relatively great, but between these regions decomposition is rapid. An examination has been made of the rates of decomposition in aqueous solutions within the pH range 3—8 ; the maximum velocity is reached around pH 5·4.[73] The final products are nitrous oxide, formaldehyde, and, presumably, water. The primary stage appears to result in the liberation of nitramine, and the methylene group is at the same time rendered accessible to oxidation by iodine and dilute alkali. The process is autocatalytic and, for individual experiments, the rate could be expressed as the sum of a unimolecular spontaneous decomposition plus a formaldehyde-catalysed bimolecular decomposition. This analysis, however, did not agree with the results of changing the methylenedinitramine concentration, and furthermore, though added formaldehyde catalysed the reaction, it did not do so as powerfully as self-generated " available formaldehyde ". The initial spontaneous decomposition is apparently dependent only on the pH of the solution, and it has been suggested [73] that the system (XXXII) (R = H for mono-ionised methylenedinitramine) is unstable, and decomposes by the route :



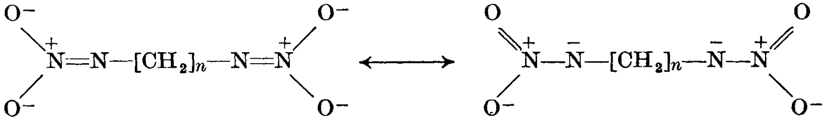
(XXXII.)

The higher members of the dinitramine series ($NO_2{\cdot}NH{\cdot}[CH_2]_n{\cdot}NH{\cdot}NO_2$; $n = 2$, 3, 4, and 5) have been known for many years. As in the series of dicarboxylic acids, there is an alternation in physical properties as the series is ascended. The second and the fourth member are relatively insoluble in water, and the melting points (for $n = 1$—5) are, respectively, 101°, 175°, 69°, 163°, and 60°. Their dissociation constants have recently

---

[73] A. H. Lamberton, C. Lindley, and J. C. Speakman, *J.*, 1949, 1650.

been compared with those of the corresponding carboxylic acids.[74] It was found that, as the series were ascended, the difference between the first and the second dissociation constants decreased more slowly in the case of the dinitramines than in that of the dicarboxylic acids. It was concluded that the distance between the charges on the double anion increased more slowly in the dinitramine series ; and it was suggested that this implied a relatively larger contribution from the canonical form (XXXIII), in comparison with (XXXIV), when $n = 1$, than when it is equal to, say, 4.



(XXXIII.) (XXXIV.)

Cyclonite and Related Compounds

The conversion of hexamine dinitrate into cyclonite (XXXV) → (XXXVI) by means of nitric acid was discovered by G. F. Henning [75] in 1899, and details of laboratory-scale processes (dealing with the nitrate, or the free base) have been given by G. C. Hale [76] and by Wright.[77] This reaction, modified by workers at the Research Department, Woolwich, to ensure continuous nitrolysis of hexamine itself on the plant scale, was in use in Britain from an early period of the war. J. H. Ross [78] has shown that cyclonite can also be obtained synthetically from formaldehyde (paraform), ammonium nitrate, and acetic anhydride. These methods were combined by Bachmann, who has given the details of a laboratory-scale preparation.[79] In the so-called " Bachmann combination process ", employed in America, an enhanced yield was obtained by the treatment of hexamine with nitric acid, acetic acid, ammonium nitrate, and acetic anhydride. The Bachmann product contains up to 10% of the eight-membered ring compound (XXXVII), of which traces are also found [80] in the Woolwich material. A review of the methods employed in Germany has been given.[81]

As was first recognised by R. P. Linstead, the degradative reaction certainly takes place in stages. Many theories have been advanced regarding the steps involved. Clearly, the original attack must involve a methylenediamine system, and if an intermediate such as (XXXVIII) is formed, the stability of the aminomethylnitramine system $[:N\cdot CH_2\cdot N(NO_2)\cdot]$ becomes involved. A number of aminomethylnitramines have been synthesised and

---

[74] C. Lindley and J. C. Speakman, *J.*, 1949, 1657.

[75] D.R.-P. 104280 (Quoted in " Thorpe's Dictionary of Applied Chemistry ", 4th Edn., Vol. 3, 535).

[76] *J. Amer. Chem. Soc.*, 1925, **47**, 2754.

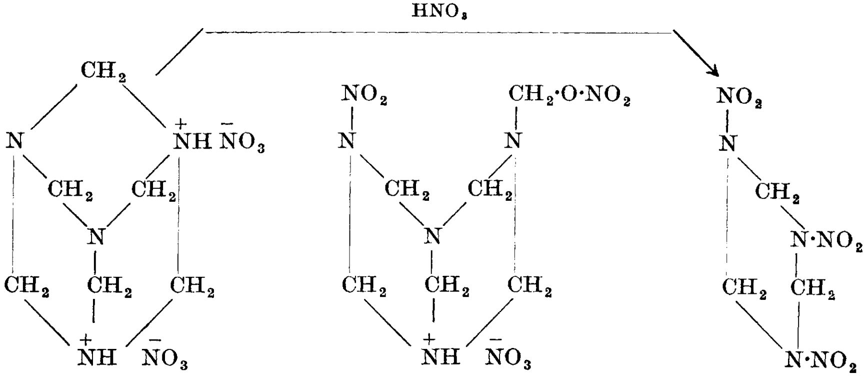
[77] W. J. Chute, D. C. Downing, A. F. McKay, G. S. Myers, and G. F. Wright, *Canad. J. Res.*, 1949, **27**, *B*, 218.

[78] Personal communication, 1940 : R. W. Schliessler and J. H. Ross, U.S.P. 2,434,230 (1948).

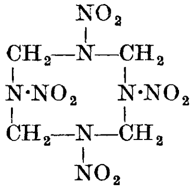
[79] W. E. Bachmann and J. C. Sheehan, *J. Amer. Chem. Soc.*, 1949, **71**, 1842.

[80] F. J. Brockman, D. C. Downing, and G. F. Wright, *Canad. J. Res.*, 1949, **27**, *B*, 469.

[81] W. de C. Crater, *Ind. Eng. Chem.*, 1948, **40**, 1632.



(XXXV.) (XXXVIII.) (XXXVI.)



(XXXVII.)

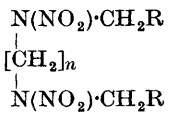
examined under the direction of R. D. Haworth at Sheffield, the work being complementary to that in progress at other centres on the degradation of hexamine itself.

Hydroxy- and Amino-methylnitramines.—Franchimont [20] showed that primary nitramines could react with formaldehyde and bases such as piperidine to yield aminomethylnitramines by a process analogous to the Mannich condensation. He found no evidence of reaction with aldehydes ($CH_3\cdot CHO$, $CCl_3\cdot CHO$, $C_6H_5\cdot CHO$) alone. It has now been shown that formaldehyde will react, and hydroxymethylnitramines of structures (XXXIX; $R = OH$; $n = 1, 3, 4$) have been prepared.[82] Ethylenedinitramine yielded only the monol (XL),[82] though the diol presumably exists in solution.[83]

With morpholine and formaldehyde aminomethylnitramines of the structures (XXXIX; $n = 2, 3,$ or 4) were obtained,[82] whilst from ethylene- or trimethylene-dinitramine, formaldehyde, and primary aliphatic amines seven- or eight-membered ring systems (*e.g.*, XLI; $n = 2$ or 3) have been produced.[83, 84] Methylenedinitramine functioned sometimes as the dinitramine, and sometimes as a precursor of nitramine: thus, under varied conditions, compounds such as (XLI; $n = 1$), (XLII), (XLIII), and (XLIV) have been isolated.[82, 84] Treatment with formaldehyde and one molecular proportion of ammonia yielded the bicyclic " D.P.T. " (XLV),[73] which is more conveniently prepared by the action of acetic anhydride on hexamine

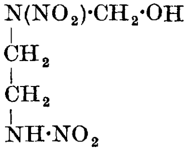
---

[82] D. Woodcock, *J.*, 1949, 1635.
[83] G. S. Myers and G. F. Wright, *Canad. J. Res.*, 1949, **27**, *B*, 489.
[84] F. Chapman, P. G. Owston, and D. Woodcock, *J.*, 1949, 1638.



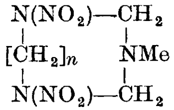
$N(NO_2){\cdot}CH_2R{-}[CH_2]_n{-}N(NO_2){\cdot}CH_2R$

(XXXIX.)

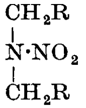


$N(NO_2){\cdot}CH_2{\cdot}OH{-}CH_2{-}CH_2{-}NH{\cdot}NO_2$

(XL.)

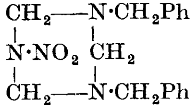


(XLI.)

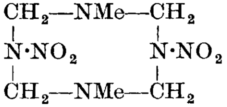


$CH_2R{-}N{\cdot}NO_2{-}CH_2R$

(XLII.)



(XLIII.)

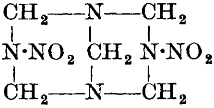


(XLIV.)

R = morpholino

dinitrate,[77] and is also formed when a solution of nitramine in an excess of aqueous formaldehyde is neutralised to pH 6 with ammonia.[77] The nitramine derivation of (XLII), (XLIII), and (XLIV) has been similarly proved by their independent synthesis from nitramine, formaldehyde, and the appropriate base.[77, 82]

Ring systems were not, of course, formed from mono-functional nitramines : thus methylnitramine, formaldehyde, and methylamine yielded the triazaheptane (XLVI).[84] Aminomethyl compounds were obtained from



(XLV.)

$CH_3{\cdot}N(NO_2){\cdot}CH_2{\cdot}NMe{\cdot}CH_2{\cdot}N(NO_2){\cdot}CH_3$

(XLVI.)

$R{\cdot}N(NO_2){\cdot}CH_2{\cdot}\overset{+}{N}HR'_2$

(XLVII.)

nitrourethane and nitrourea, but hydroxymethyl compounds could not be isolated.[85]

The formation and properties of such compounds have been discussed [85] in terms of the reversible equations (M), (N), and (O).

(M) $R{\cdot}NH{\cdot}NO_2 + CH_2O \rightleftharpoons R{\cdot}N(NO_2){\cdot}CH_2{\cdot}OH$

(N) $R'_2NH + CH_2O \rightleftharpoons R'_2N{\cdot}CH_2{\cdot}OH$

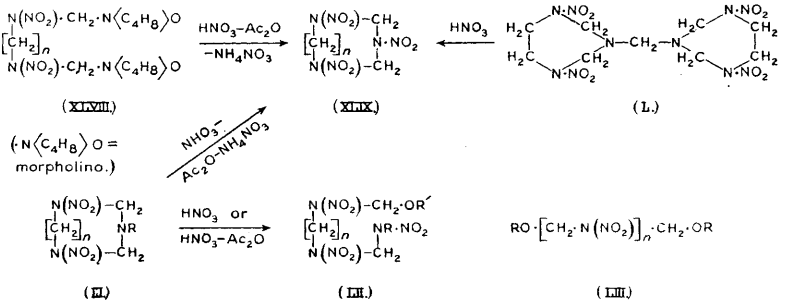
(O) $R{\cdot}NH{\cdot}NO_2 + CH_2(OH){\cdot}NR'_2 \rightleftharpoons R{\cdot}N(NO_2){\cdot}CH_2{\cdot}NR'_2 + H_2O$

It has been concluded (on the evidence of ordinary and potentiometric titrations with alkali, and of the determination, by various reagents, of available formaldehyde) that on dissolution of the hydroxymethylnitramines in water the equilibrium (M) is rapidly established, and probably lies well to the left : the hydroxymethylnitramines may be more stable in the presence of acids. On similar grounds the aminomethylnitramines are found to be largely decomposed in aqueous solution, but they are stabilised if the solid compounds are dissolved in 2N-mineral acids : apparently the cation (XLVII) is formed (cf., also, XXIX). The aminomethylnitramines are often sparingly soluble, and dissolve more readily in polar than in non-polar solvents. In this, as in other properties, they differ markedly from the formally

---

[85] A. H. Lamberton, C. Lindley, P. G. Owston, and J. C. Speakman, *J.*, 1949, p. 1641.

similar nitroparaffin condensation products. The hydroxy- and aminomethylnitramines are, in chemical properties, more nearly related to the cyanohydrins and aminomethyl cyanides: all of these compounds may be expressed by the general formula $X\cdot CH_2\cdot OH$ or $X\cdot CH_2\cdot N<$, and their behaviour is comparable in terms of the strength of the acid HX. The Sheffield authors [85] were thus of the opinion that Lapworth's work [86] on cyanohydrins and aminomethyl cyanides was here applicable, and that therefore hydroxymethylnitramines will lose a proton readily (*e.g.*, as on titration) but will resist the elimination of a hydroxyl ion. This speculation is supported by the failure of many workers to prepare cyclonite from formaldehyde and nitramine.* [87] The reaction $—N(NO_2)\cdot CH_2\cdot OH + HN< \rightarrow —N(NO_2)\cdot CH_2\cdot N< + H_2O$, also, was held to proceed indirectly by decomposition (equation M), union of the liberated formaldehyde with the amine (equation N) and, finally, condensation (equation O). A. F. McKay and Wright,[77] however, favour the direct union of hydroxymethylnitramine and base: experimental evidence is not yet available.



Treatment of the open-chain aminomethylnitramines (XLVIII; $n = 2$ or 3) with nitric acid, acetic anhydride, and ammonium nitrate led to elimination of the morpholine portion of the molecule, with some recovery as nitromorpholine; and ring synthesis took place by insertion of a nitramino-group.[88] "Homocyclonite" (XLIX; $n = 2$) was in fact first prepared [83] by nitrolysis of (L), a condensation product of ethylenedinitramine, formaldehyde, and ammonia. The yield (74%) obtained by the synthetic route is remarkable: the eight-membered ring (XLIX; $n = 3$) was similarly prepared in good yield, but the nine-membered ring could not be obtained.[88]

When the cyclic aminomethylnitramines (LI; R = alkyl) were treated with nitric acid alone, ring cleavage took place and the nitrate esters (LII;

---

[86] *J.*, 1930, 448; 1931, 1387.

[87] Personal communications.

[88] F. Chapman, *J.*, 1949, 1631.

* The argument is very possibly inapplicable to solutions in concentrated acids. Note, also, *N*-nitrofurfuraldimine (p. 76).

$R' = NO_2$) were produced : if acetic anhydride was present the acetates (LII ; $R' = Ac$) were isolated.[89] In the presence, additionally, of ammonium nitrate the same cleavage took place in some cases : in others the cyclic trinitramine (XLIX) was produced. In no case was a cyclic compound obtained without the use of ammonium nitrate, and as, for example, " homocyclonite " (XLIX ; $n = 2$) could also be obtained from (XLVIII), the reaction possibly proceeded by fragmentation followed by synthesis, rather than by replacement. The presence of amino-nitrogen, in some form, seems to be essential for the synthetic completion of nitramino-ring systems. Thus cyclonite has been produced by heating paraformaldehyde with ammonium nitrate and nitric acid,[72] but not, as yet, from nitramine and formaldehyde.[87]

The Linear Polymethylenenitramines.—A number of compounds of the general type (LIII ; $n = 1$, 2, 3, or 4) have been prepared in the course of recent researches,[77, 79, 82, 90, 91] and many investigations are as yet unpublished. Wright has pointed out that these linear esters ($R = Ac$ or NO_2) commonly result from nitrolyses in which the medium contains the corresponding anhydride (*e.g.*, Ac_2O or N_2O_5) but not ammonium nitrate ; and some members (*e.g.*, " B.S.X." : LIII ; $n = 3$, $R = Ac$) are readily accessible by this, or other, techniques.[79, 91] Their chemistry is interesting, yet simple. The nitrate esters ($R = NO_2$) can be converted into the ethers (R = alkyl) or the acetates ($R = Ac$) by warming with, respectively, an alcohol, or sodium acetate in acetic acid. The chain is resistant to anhydrous nitric acid, which reconverts the ethers and acetates into the nitrates.

The Nitrolysis of Hexamine

Of many conflicting theories, only those of the Toronto school have as yet been published, though an initial paper from Bachmann has been noted.[79] From considerable experience at Bristol,[72] A. Carruthers [92] has set down his opinions regarding the Woolwich process. All available evidence [such as the measurement of heats of reaction, and the facile production of the salt (XXIX)] indicates that nitrolyses involving the formation of two nitramino-groups occur very rapidly. Attack on the hexamine dinitrate cage system (XXXV) is postulated to yield (LIV ; $R = H$), which is quickly esterified ($R = H \longrightarrow R = NO_2$: formula now the same as XXXVIII). The second nitrolysis may occur by rupture at A, B, or C ; and the available evidence definitely favours attack at B to yield (LV ; $R = H \longrightarrow NO_2$) as the main route in the production of cyclonite. Fission at C would give rise to the tetramer (XXXVII). Owing to the symmetry of the system, these arguments will not be invalidated if the nitro-group adds on to the tertiary instead of the quaternary nitrogens (p. 83).

Wright [77] has shown that if the nitrolysis liquor is neutralised with

---

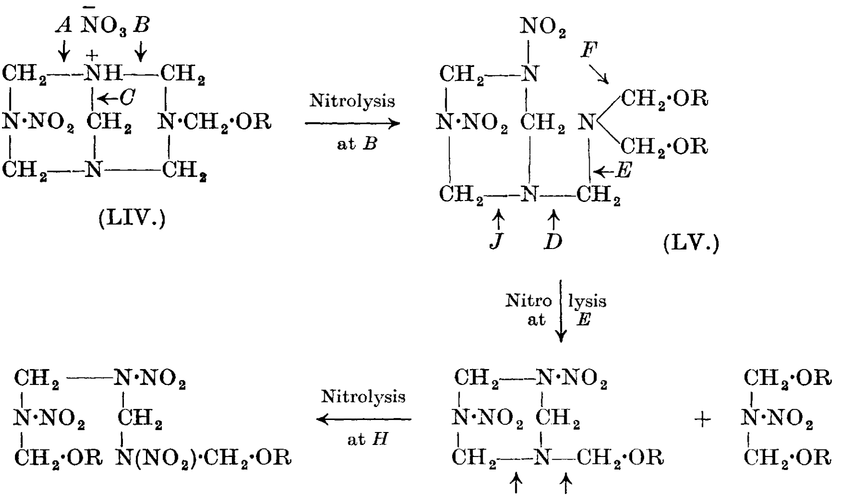
[89] F. Chapman, P. G. Owston, and D. Woodcock, *J.*, 1949, 1647.

[90] A. F. McKay, H. H. Richmond, and G. F. Wright, *Canad. J. Res.*, 1949, **27**, *B*, 462.

[91] W. J. Chute, A. F. McKay, R. H. Meen, G. S. Myers, and G. F. Wright, *ibid.*, p. 503.

[92] Personal communication, April, 1944.

ammonia,* " D.P.T." (XLV) is formed. This must be due to synthesis subsequent to neutralisation, since, though " D.P.T." dissolves in acid, it is reprecipitated at a smaller pH than that necessary for its initial preparation. The requisite nitramine ($NH_2{\cdot}NO_2$) cannot persist under acid conditions, but it was shown that the addition of formaldehyde stabilised nitramine in acid (see also ref. 85); and it is therefore suggested that dihydroxymethylnitramine (LVI; R = H), produced by nitrolysis of (LV) at *E*, is the precursor of " D.P.T." The main incidence of nitrolysis, however, is postulated at *D*, to yield cyclonite.[83] Carruthers postulates a different behaviour of compound (LV): hydrolysis may occur at *D* to yield the salt (XXIX), known to be readily convertible into cyclonite; or nitrolysis at *F* may precede the hydrolysis at *D*. Both routes yield cyclonite, and the production of dihydroxymethylnitramine (LVI; R = H) (or its ester) is a measure of the extent to which the second process takes place.



(LIV.) (LV.) (LVIII.) (LVII.) (LVI.)

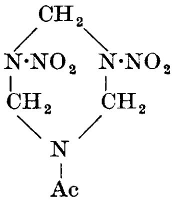
Wright [83, 91] holds that esterification of the terminal $CH_2{\cdot}OH$ groups is a critical factor. He considers that while anhydrides (*e.g.*, Ac_2O or N_2O_5) naturally favour esterification, ammonium nitrate has the reverse effect: it may do so either directly, or by promoting the removal of formaldehyde (" demethylolation ") before esterification can take place. Incidentally, acetic anhydride and nitric acid appear to react separately, and cannot be replaced by acetyl nitrate, when absence of acetic acid precludes the reaction $AcO{\cdot}NO_2 + AcOH \rightleftharpoons Ac_2O + HNO_3$.[90] After esterification, the preferential course of nitrolysis is changed. Thus, under Bachmann's conditions (both Ac_2O and NH_4NO_3), the compound (LV; R = H) may be " demethylolated " and subsequently nitrolysed at *D* to yield cyclonite. If esterification wins the race [as when the ratio Ac_2O/NH_4NO_3 is high [91]] the compound (LV; R = Ac) may be nitrolysed at *E* to yield (LVII;

---

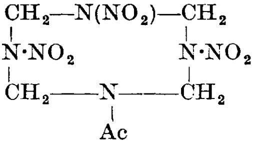
* Other alkalis will serve, since ammonium nitrate is present in the nitrolysis liquor.

R = H) and (LVI ; R = Ac) : the latter compound has been isolated.* Similar processes may again ensue. If (LVII) is attacked before esterification, rupture at *G* gives more cyclonite : if not, scission at *H* yields, finally, the linear " B.S.X." (LVIII ; R = Ac).[79] Linear tetramers may be produced by successive nitrolyses of (LV) at *F* and *J*. Space precludes the presentation of the evidence : as none of the compounds (LV ; R = H, Ac, or NO_2) has ever been isolated, it is inferential in character and is based on the behaviour of " D.P.T." and of " homocyclonite " (XLV ; and XLIX, $n = 2$). Furthermore, it may be necessary to consider ammonium nitrate in a synthetic rôle (pp. 94, 95).

In the Bachmann combination process (p. 91) there is need to consider not only the degradation of hexamine, but also the utilisation of the formaldehyde fragments which are lost, mainly as methyleneglycol dinitrate, in the Woolwich process. There are two major possibilities. Either cyclonite is synthesised *per se* from fragments or, in the Ross (p. 91) and hence also in the Bachmann process, hexamine is first synthesised and subsequently degraded.† The major evidence for the direct synthesis of cyclonite is that addition of methylenedinitramine (XXX) can enhance the yield of the Ross process to an extent greater than could be explained from its methylene content alone.[93] Carruthers and J. K. N. Jones [72] have demonstrated the same effect in a hexamine–nitric acid system, and in their preparation of cyclonite from paraform, ammonium nitrate, and nitric acid.



(LIX.)



(LX.)

Nevertheless, Wright [93] favours the second hypothesis. The evidence, briefly, is that two by-products, (LIX) and (LX), of invariable occurrence in the Ross and in the Bachmann process, have been independently prepared from derivatives of hexamine : up to the present these derivatives have been obtained only from pre-formed hexamine, and never by independent syntheses. The favourable influence of methylenedinitramine is ascribed to its action in holding formaldehyde (as XXXIX ; $n = 1$, R = OH) ‡ until required for the synthesis of hexamine ; and it is suggested that

---

[93] E. Aristoff, J. A. Graham, R. H. Meen, G. S. Myers, and G. F. Wright, *Canad. J. Res.*, 1949, **27**, *B*, 520.

* The isolation of (LVII ; R = Et) has provided evidence of the existence, at least, of (LVII ; R = NO_2) ; ref. 72 and K. W. Dunning and W. J. Dunning, *J.*, 1950, 2920.

† Nitric acid for degradation in the Ross reaction would be produced from ammonium nitrate in the course of hexamine synthesis.

‡ It must indeed, if it plays any part, be hydroxymethylated ; free methylenedinitramine is destroyed very rapidly by concentrated acids.

this retention prevents the irretrievable loss of formaldehyde as methylene diacetate, which was found, experimentally, to be incapable of furnishing methylene groups for the synthesis of cyclonite.

Though the Reviewer disclaims either the ability or the desire to review critically the whole range of recent research on cyclonite and allied compounds—or even to deal fully, in the space available, with that portion which has been published—some comments upon the major implications of this work are perhaps permissible in conclusion. It is now clear that the nitration of amines and of amides is not completely analogous to either aromatic or aliphatic nitration on a carbon atom, and that the products differ fundamentally from the *C*-nitro-compounds. The remarkable (chemical) stability, at least towards acidic reagents, of both the linear and the cyclic polymethylenenitramines has been revealed. Finally, the occurrence and ready synthesis of seven- and eight- (but not of nine-) membered ring systems deserves notice. Though no explanation of this feature has yet been given, it may be borne in mind that, as the group is planar, the normal $C{-}N(NO_2){-}C$ angle may be larger than 109°, and the ring structures more nearly planar than those of the corresponding carbocyclic compounds. It remains to be seen whether this is the case ; and, if so, if the fact is relevant.

The Reviewer's thanks are due to the Principal Director of Scientific Research (Defence) for permission to include unpublished material ; and also to Dr. T. S. Stevens and Mr. J. Barrott for helpful criticism.