322. *The Nitration of Dimethylaniline to Tetryl, 2 : 4 : 6 :* N*-Tetranitromethylaniline. The Course of the Reaction.*

By C. E. CLARKSON, I. G. HOLDEN, and T. MALKIN.

The formation of tetryl from dimethylaniline proceeds in two main stages: (1) dimethylaniline ⟶ 2 : 4-dinitrodimethylaniline, (2) 2 : 4-dinitrodimethylaniline ⟶ tetryl, the latter stage proceeding largely *via* 2 : 4-dinitromonomethylaniline, but also *via* dimethylpicramide.

Stage (1) is catalysed by nitrous acid, probably owing to the production of nitronium ions from dinitrogen tetroxide, $N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-$ (cf. Addison and Thompson, *J.*, 1949, S 211; Levy and Scaife, *J.*, 1946, 1093).

Stage (2) is accelerated in a different manner by nitrous acid, which is found to be a powerful demethylating agent. The mechanism of the transformation 2 : 4-dinitrophenylnitramine ⟶ methylpicramide is discussed.

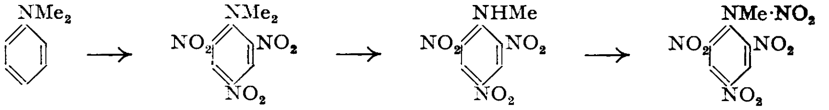
TETRYL was first prepared by Mertens (*Ber.*, 1877, **10**, 995) as yellow crystals, m. p. 127°, by boiling dimethylaniline with fuming nitric acid, but he was unable to obtain satisfactory analytical results, presumably because of the explosive properties. A little later its constitution was established by van Romburgh (*Rec. Trav. chim.*, 1883, **2**, 103; 1889, **8**, 215) who found that tetryl could be prepared by the nitration of both methyl- and dimethyl-aniline, and, from the fact that carbon dioxide and oxides of nitrogen were evolved profusely in the latter case, but not appreciably in the former, he concluded that tetryl contained only one methyl group; this he confirmed by preparing tetryl from *N*-methyl- and *NN*-dimethyl-picramide, and by synthesis from picryl chloride and potassium methylnitramine.

Tetryl has long been used both as a high explosive and as an initiator or primer for high explosives and propellants, and there is much information on its preparation [Langscheidt, *Z. ges. Schiess. u. Sprengstoffw.*, 1912, **7**, 445; van Duin, *Rec. Trav. chim.*, 1917, **37**, 111; Wride, *Arms and Explosives*, 1923, **28**, 6; Tanner, *Chem. Met. Eng.*, 1923, **29**, 404; Desvergnes, *Mem. Poudres*, 1922, **19**, 217; Bain, *Army Ordnance*, 1926, **6**, 435; Attillio Izzio, (*Review*) *Industria chimica*, 1933, **8**, 171; Chao Lung Tseng and Tu Chi Lin, *J. Chem. Eng. China*, 1933, **2**, 128; Desvergnes, *Chim. et Ind.*, 1930, **24**, 785; Nolan and Clapham, *Sci. Proc. Roy. Dublin Soc.*, 1923, **17**, 219).

The only practicable method of preparation is the nitration of dimethylaniline, and most of those studied by the observers noted above involve the addition of a solution of dimethylaniline in concentrated sulphuric acid (referred to subsequently as D.M.A.S.) to nitric acid, or to a mixture of nitric and sulphuric acids, under a variety of conditions of concentration and temperature. The nitration of methylaniline, which would appear to be a more direct route, gives a much lower yield (75% compared with 93%), owing mainly to *meta*-nitration, leading to 2 : 3 : 4 : 6 : *N*-pentanitromethylaniline or " meta-tetryl " (cf. Knowles, *Ind. Eng. Chem.*, 1920,

12, **246**; Forster and Coulson, *J.*, 1922, **121**, 1988), a particularly undesirable impurity which catalyses the decomposition of tetryl (Hinshelwood, *J.*, 1921, **119**, 721).

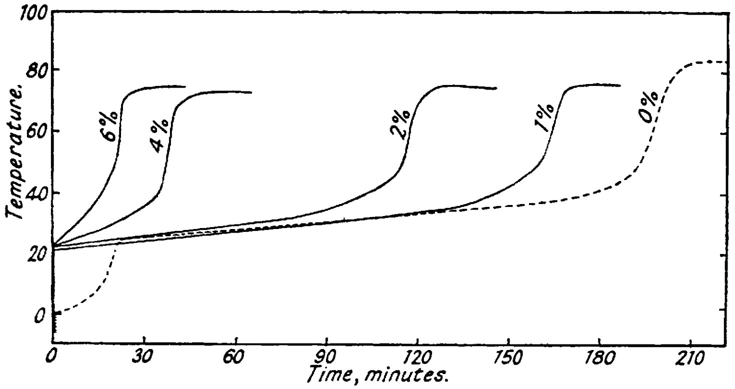
Of the methods referred to above, that of Wride is of interest in that he recognised two main stages in the reaction. In the first stage he added D.M.A.S. to a nitrating mixture of nitric and sulphuric acids, keeping the temperature at 45°, and in the second, he warmed the solution to 65° and maintained it at this temperature until the reaction was complete. Wride considered that stage I was conversion into dimethylpicramide, and that stage II was oxidation and nitration of this to tetryl, *viz.* :



In this view, generally accepted hitherto, Wride was, however, only partly correct, for on plotting a time–temperature curve of the reaction after mixing D.M.A.S. with nitrating acid in a Dewar vessel (Fig. 1, for which we are indebted to Drs. H. D. Springall and T. H. Bevan) it is seen, in agreement with Wride, that there are two main stages, but on drowning the reaction mixture with water, after the completion of the first stage, one obtains an almost quantitative yield of 2 : 4-dinitrodimethylaniline.

FIG. 1.

The effect of nitrous acid on the speed of formation of tetryl.



D.M.A.S. and nitrating acid containing the above percentages of nitrous acid mixed at —7°.

Time–temperature curves taken as indicated above show that the presence of nitrous acid increases the rate of both stages of the reaction (Figs. 1 and 2; Drs. Springall and Bevan, unpublished). The type of effect seems to be different in the two stages, since very small amounts affect stage I; for example, any amount above 0·3% in the nitrating acid makes stage I practically instantaneous, whereas increasing amounts up to 6% still further increase the rate of stage II. One gains the impression that in stage I the action is catalytic, whilst in stage II nitrous acid is a reactant rather than a catalyst.

Before dealing with these stages in detail, it will assist later discussion if the main facts of a tetryl preparation are described. D.M.A.S. is added with vigorous stirring to nitrating acid in a flask surrounded by ice, and the temperature is not allowed to exceed 30—35°. The first drop of D.M.A.S. produces a deep red colour which is intensified as the addition proceeds. After the addition, the reaction flask is surrounded by a water-bath at 90—100°, which is removed when the contents of the flask reach 60°, from which point the temperature rises at a convenient rate without external heat. During this rise, the reddish-orange solution becomes darker and less clear, and at a little above 70° assumes a purplish colour. At this stage, tetryl begins to separate as an oil, and soon solidifies in a fine crystalline form, the separation being accompanied by a violent evolution of brown fumes (fume-off) and a rapid rise in temperature, which should not be allowed to exceed 100° (ice-bath).

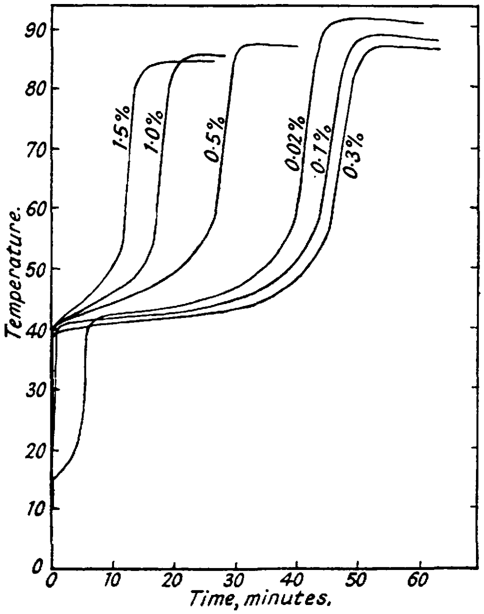
Stage I. Dimethylaniline ⟶ 2 : 4-*Dinitrodimethylaniline.*—Dinitration is rapid and it is difficult to isolate the mononitro-compound. If, however, the reaction is carried out at —20°

and the reactants are poured into cold alkali, it is possible to isolate a small amount of *p*-nitrodimethylaniline (unpublished work by Dr. T. H. Bevan).

The main point of interest in this stage is the action of traces of nitrous acid, which appears to be catalytic. Martinsen (*Z. physikal. Chem.*, 1904, **50**, 385; see also Benford and Ingold, *J.*, 1939, 931, for fuller references) has observed a similar effect in the nitration of phenol, and he considers, but rejects, the view that rapid nitrosation, followed by oxidation, is the explanation. Unpublished work by Dr. H. D. Springall has shown that this view cannot be supported in the present case, since *p*-nitrosodimethylaniline gives a much lower yield of tetryl than does dimethylaniline.

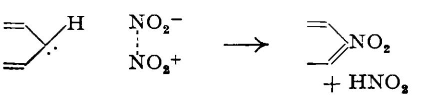
FIG. 2.

The effect of nitrous acid on the speed of formation of tetryl.

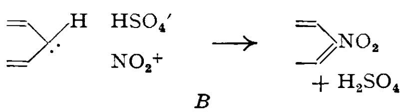


D.M.A.S. and nitrating acid containing the above percentages of nitrous acid mixed at 10°.

The catalytic action may be due to ionization or even potential ionization of dinitrogen tetroxide to NO_2^- and NO_2^+, the latter nowadays being regarded as a powerful nitrating agent (Bennett, Brand, and Williams, *J.*, 1946, 869). Such ionization would provide additional nitronium and proton acceptors in the nitrating system. Alternatively, if ionization takes place only on approach of dinitrogen tetroxide to an active aromatic centre, the velocity of nitration might be expected to be increased since only a bimolecular collision, *A*, would be required instead of the termolecular collision needed for normal nitration, *B* :



A



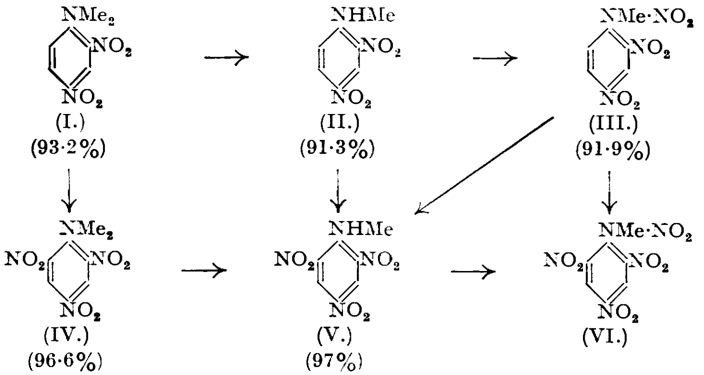
B

The important point is that the concentration of nitrous acid is not reduced by this process :

$$2HNO_2 \longrightarrow N_2O_3 \longrightarrow NO + NO_2 \xrightarrow{HNO_3} N_2O_4 \longrightarrow NO_2^- + NO_2^+$$

Thus for each molecule nitrated, one molecule of nitrous ion is produced, and one molecule of nitric acid is reduced to nitrous acid.

Stage II. 2 : 4-*Dinitrodimethylaniline* ⟶ *Tetryl*.—When at this stage the mixture was poured into water at different intervals, the only intermediate isolated was 2 : 4-dinitromonomethylaniline, and therefore the course of the reaction must be arrived at indirectly. Possible routes are given in the following scheme, and from a consideration of the observed yield of tetryl from each intermediate, given in parentheses, it is possible to deduce the main course of the reaction.



Thus, a 93·2% yield of tetryl from (I) can be obtained either by a combination of routes (*a*) and (*b*), or by route (*b*) exclusively, assuming a loss in yield in stage I ⟶ IV :

$$\begin{tikzcd}
 & & \mathrm{III} \arrow[d] \arrow[dr] & \\
(a)\ \mathrm{I} \arrow[r] & \mathrm{II} \arrow[ur] \arrow[dr] & & \mathrm{VI} \\
 & & \mathrm{V} \arrow[ur] &
\end{tikzcd}$$

$$(b)\quad \mathrm{I} \longrightarrow \mathrm{IV} \longrightarrow \mathrm{V} \longrightarrow \mathrm{VI}$$

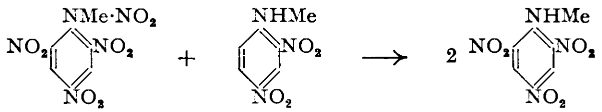
The evidence is against the latter view, since (II) is the only intermediate that can be isolated. Moreover, the acceleration of this stage of the reaction by nitrous acid (Fig. 2), which is found to be a powerful demethylating agent, suggests the early formation of (II); and, finally, the production of a purple colour, which is a striking feature of tetryl preparations, is a well-known property of nitramines in the presence of concentrated sulphuric acid (Orton, *J.*, 1902, 806; Orton and Smith, *J.*, 1905, 389). If, then, there is no appreciable loss in the conversion (I ⟶ IV), the yield of tetryl from (I) corresponds to a combination of (*a*) and (*b*) in the proportion of 1·8 to 1·0.

The main course of route (*a*) appears to be

$$\mathrm{I} \longrightarrow \mathrm{II} \longrightarrow \mathrm{III} \longrightarrow \mathrm{V} \longrightarrow \mathrm{VI},$$

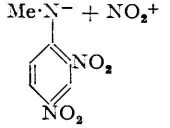
for we find it possible to convert (II) into (III) in 94% yield by means of concentrated nitric acid (70%), whereas all attempts to prepare (V) from (II) have failed. Moreover, the conversion of (II) into tetryl is always accompanied by the characteristic violet colour. This we consider is an indication of the intra(? inter)-molecular change (III ⟶ V). Aromatic nitramines are known to undergo intramolecular changes readily in the presence of sulphuric acid (Bamberger, *Ber.*, 1897, **30**, 1253; Orton and Smith, *loc. cit.*), and, in agreement with this, (III) can be converted by means of sulphuric acid into (V) in 90% yield. Moreover, (III) is always converted into tetryl more readily by a mixture of nitric and sulphuric acids than by nitric acid alone.

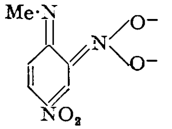
Arising out of the reactions in route (*a*) are the interesting points concerning the nature of the purple colour, and the mechanism of the change (III ⟶ V). On the latter question, our results lead us to somewhat the same conclusions as those of Bradfield and Orton (*J.*, 1929, 917), who studied the transformations of simple aromatic nitramines and considered their evidence to be in harmony with an intramolecular process, although they also obtained evidence of extranuclear migration of nitro-groups. We, too, find evidence for the latter. Thus, equimolecular amounts of tetryl and 2 : 4-dinitromonomethylaniline, when kept overnight in concentrated sulphuric acid, yield methylpicramide almost quantitatively :

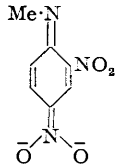


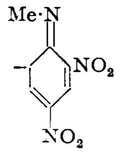
No extranuclear migration takes place, however, when 2 : 4-dinitrophenylmethylnitramine and *p*-nitromonomethylaniline or 2 : 4-dinitrodimethylaniline are similarly treated, the nitramine merely changing into methylpicramide.

These results, in conjunction with the production of the purple colour, suggest the possibility of an ionic mechanism. Dinitrophenylmethylnitramine, in a medium of high dielectric constant, for example, nitrating acid, might ionize to (VII), which could exist in the canonical forms (VIII, IX, and X), which would be expected to be highly coloured :


(VII.)

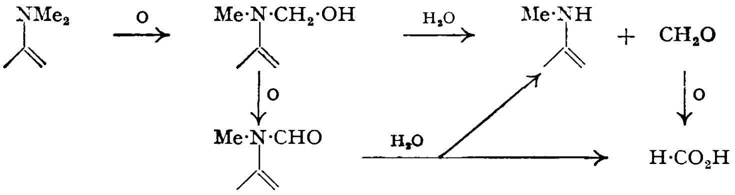

(VIII.)


(IX.)


(X.)

This ionization produces a planar, highly resonating system, with a consequent gain in stability, and therefore has some degree of probability. In the presence of nitronium, (X) will be nitrated in the *ortho*-position to yield the highly symmetrical trinitro-ion, but at this stage the solubility factor comes into play and this ion combines with nitronium to form tetryl, which is precipitated. An ionic mechanism of this kind, which implies an almost instantaneous reaction from dinitromonomethylaniline, would explain the difficulty of isolating any other intermediate. On the above view, the distinction between an inter- and an intra-molecular reaction is extremely fine, and whilst a nitronium ion at the moment of dissociation is likely to be the nearest to the vacant *ortho*-position it would not necessarily be so.

Demethylation of 2 : 4-*Dinitrodimethylaniline.*—The accelerating effect of nitrous acid in the second stage of the tetryl reactions led us to investigate the action of nitrous acid on 2 : 4-dinitromethylaniline, and we found that it is an effective demethylating agent, converting the latter, in 65% sulphuric acid, rapidly in the cold, into 2 : 4-dinitrophenylmethylnitrosamine. Comparative tests show that nitrous acid is a much more rapid demethylating agent than nitric acid. Both formaldehyde and formic acid have been identified as products of demethylation, which appears to proceed through the following stages :



We have no evidence that would indicate the presence of methyl alcohol at any stage of the demethylation, and we have not observed even traces of esters of nitric or nitrous acid.

Formic acid can be isolated from the tetryl reaction in large amounts, if the temperature is not allowed to exceed 60°, and its decomposition by nitrating acid at higher temperatures is the main cause of the characteristic " fume-off."

EXPERIMENTAL.

Preparation of Tetryl.—Our work was primarily undertaken to determine the optimum conditions for the continuous production of tetryl in high yield and quality, the latter being of great importance for service material, which has to pass stringent tests for stability (cf. Farmer, *J.*, 1920, **1433**, **1602**). The following concentrations of D.M.A.S. and nitrating acid were found suitable. Concentration of the two acids were variable over a small range, but the water content, calculated on the mixed D.M.A.S. and nitrating acid, should not vary by more than ±2%.

Preparation of D.M.A.S. Dimethylaniline (60 c.c.) was run into 96% sulphuric acid (180 c.c.) with vigorous stirring and ice-cooling, the temperature being kept below 30° (local heating can give rise to tetramethylbenzidine ; the acid concentration is not significant, but was used for technical reasons).

Nitrating acid. 99% Sulphuric acid (360 c.c. ; *d* 1·84) was added to ice (250 g.), with external cooling, and 98% nitric acid (227 c.c. ; *d* 1·5) added with stirring. Nitrating acid made with ordinary 70% nitric acid always gave a slightly lower yield of tetryl.

Nitration. The main details of the preparation have been given in the Introduction. A convenient laboratory scale is to add 60 c.c. of D.M.A.S. to 240 c.c. of nitrating acid in a 1-l. round-bottom " Quickfit " flask, fitted with three necks to take a dropping funnel, a thermometer, and a stirrer. After the addition of D.M.A.S., the dropping funnel is replaced by a wide reflux-tube to take off the fumes, and the experiment should be carried out only in a most efficient fume chamber.

After the " fume-off " already described, and when it is clear that the temperature of the reaction is falling, the reaction vessel is heated in a water-bath for half an hour to clarify the solution and expel oxides of nitrogen. After cooling to room temperature the tetryl is filtered off through a sintered-glass funnel and well washed with water.

" *Steam blowing.*" The simplest way of purifying tetryl is to suspend it in 500 c.c. of water in a 1½-l. flask and pass steam through it for half an hour. This removes surface and occluded acid, and converts any "meta-tetryl" and other impurities into the water-soluble "meta-hydroxytetryl" (3-hydroxy-2 : 4 : 6 : *N*-tetranitromethylaniline) and picric acid, respectively. After cooling, tetryl is filtered off, washed with water, and dried in the air on filter-paper trays. In a good experiment the wash-water should be just faintly yellow. Yield, 92—93%; m. p. 128·5—129°. Tetryl crystallises from alcohol and aqueous acetone.

2 : 4-*Dinitrodimethylaniline.*—The above D.M.A.S. (60 c.c.) was slowly added with stirring to nitrating acid (240 c.c.), the temperature being kept below 30°. After 5 minutes, the dark red solution was poured into water (2·5 l.) with stirring, and the orange-yellow granular precipitate filtered off, dried, and crystallised from alcohol containing a little acetone. The yield was practically quantitative. 2 : 4-Dinitrodimethylaniline crystallises in two forms: fine needles, m. p. 77°, and truncated octahedra, m. p. 87°.

This experiment is merely the first stage of a tetryl preparation, and the quantitative yield of dinitro-compound is confirmed by the fact that both the latter and dimethylaniline give the same final yield of tetryl. The above preparation uses a large excess of nitrating acid, and twice the amount of D.M.A.S. can be used if the reaction is to be used as a preparation of the dinitro-compound.

Action of Nitrous Acid on 2 : 4-*Dinitrodimethylaniline.*—2 : 4-Dinitrodimethylaniline (2 g.) was dissolved in 65% sulphuric acid (20 c.c.) with gentle warming, and to the cold solution sodium nitrite (3 g.) was added in small quantities with stirring and cooling. A light-yellow precipitate quickly formed, and was filtered off, washed, and dried (1·8 g.; m. p. 83°). Crystallised from alcohol, it separated in yellow hexagonal plates, m. p. 85°, giving no depression with an authentic specimen of 2 : 4-dinitro-*N*-nitrosomonomethylaniline. If the temperature is allowed to rise, 2 : 4-dinitromonomethylaniline is the main product.

Isolation of Formic Acid from a Tetryl Preparation.—In order to facilitate isolation of the formic acid, conditions were chosen to give a large excess of D.M.A.S. and so reduce to a minimum the amount of nitrous and nitric acids present. D.M.A.S. (60 c.c.) was slowly added with stirring and cooling to standard nitrating acid (76 c.c.; 240 c.c. required for a normal tetryl preparation), and the temperature was not allowed to rise above 45°. After several hours at this temperature, tetryl began to separate. After being kept overnight, this was filtered off, and the filtrate was diluted with 4—5 times its bulk of water and filtered from a reddish tarry precipitate. After treatment with ferrous sulphate solution and filtration, the liquid was steam-distilled. *ca.* 2 l. of distillate were neutralised with aqueous sodium hydroxide and evaporated to dryness, to yield 2 g. of sodium formate, which responded to all the usual tests, including conversion into oxalate. This yield is ≃ 80%, calculated on the amount of tetryl formed.

Preparation of 2 : 4-*Dinitromonomethylaniline* (private communication from Dr. J. K. N. Jones).—2 : 4-Dinitrodimethylaniline (20 g.) was refluxed with dilute nitric acid (19 c.c. of HNO_3, *d* 1·42, in 200 c.c. of water) until the heavy oily layer changed to the solid dinitromonomethylaniline (about 1 hour). The reaction mixture was then cooled and filtered; the product, crystallised from acetone, had m. p. 178° (yield, practically quantitative).

When a current of air was passed through the reaction mixture, formaldehyde was detected, by smell and by formation of the 2 : 4-dinitrophenylhydrazone (Dr. Jones informs us that the corresponding diethyl derivative behaves similarly, yielding acetaldehyde).

2 : 4-*Dinitrophenylmethylnitramine.*—2 : 4-Dinitromonomethylaniline (5 g.) was added to 70% nitric acid (100 c.c.; *d* 1·42) and gently warmed to about 40° to complete dissolution. After storage in water at room temperature for 2½ hours, the solution was poured into 800 c.c. of water, a light yellow granular precipitate separating. This was filtered off, washed, and dried (5·1 g.), having m. p. 111°, raised to 115° by crystallisation from alcohol. The *nitramine* crystallised in light yellow hexagonal prisms (Found: C, 34·3, 34·4; H, 2·63, 2·66; N, 22·0, 21·7. $C_7H_6O_6N_4$ requires C, 34·7; H, 2·5; N, 23·1%).

The structure was confirmed by removal of the *N*-nitro-group by heating the substance with phenol to yield 2 : 4-dinitromonomethylaniline (cf. Mertens, *Ber.*, 1886, **19**, 2123, and Romburgh, *Rec. Trav. chim.*, 1886, **5**, 240).

This nitramine and the isomeric methylpicramide have the same m. p., which may explain why the former has not previously been described. We consider it probable that the product obtained by Hodgson and Turner (*J.*, 1942, 584) by the action of 70% nitric acid on dimethylaniline, and thought to be methylpicramide, was actually 2 : 4-dinitrophenylmethylnitramine.

Conversion of 2 : 4-*Dinitrophenylmethylnitramine into Methylpicramide.*—The nitramine (0·2 g.) was dissolved in concentrated sulphuric acid (2 c.c.), and the solution was diluted with water (1·5 c.c.) Some material was first precipitated but dissolved again as the temperature rose. After a few minutes the solution was diluted with water; the resulting precipitate, filtered off and dried (yield, 0·18 g.), had m. p. 111—112° (mixed m. p. with original nitramine, 85°; mixed m. p. with methylpicramide, 113—114°).

Yield of Tetryl from Possible Intermediates.—(1) *From* 2 : 4-*dinitrodimethylaniline.* The dinitro-compound (5 g.) was dissolved in 75% sulphuric acid (50 c.c.), and 98% nitric acid (11 c.c.) was added with stirring, the temperature being kept below 40°. Sodium nitrite (0·05 g.) was then added, and the reaction was then continued as described for the standard tetryl preparation. The product was steam-blown and dried. The yield was 6·4 g. (93·2%).

(2) *From* 2 : 4-*dinitromonomethylaniline.* The dinitro-compound (5 g.) was treated as in (1). There was no appreciable " fume-off." The yield was 6·65 g. (91·3%).

(3) *From* 2 : 4-*dinitrophenylmethylnitramine.* 2 G. of this substance were heated with 24 c.c. of nitrating acid of composition H_2SO_4 64, HNO_3 15, H_2O 21%, and the nitration completed as in (1), the yield being 2·18 g. (91·9%).

(4) *From monomethylpicramide.* 1 G. of this material was nitrated under the same conditions as in (3), *i.e.*, 12 c.c. of nitrating acid of the same strength. The yield was 1·15 g. (97%).

(5) *From dimethylpicramide.* 2 G. of the substance, nitrated as in (3), gave 2·165 g. (96·6%).

Inter- and Intra-molecular Changes.—(*a*) Tetryl (1·46 g.) in cold concentrated sulphuric acid (10 c.c.)

was added to 2 : 4-dinitromonomethylaniline (1 g.) in the same solvent (10 c.c.) (equimolecular proportions of reactants). After being kept overnight, the solution was poured into water, and the light-orange precipitate filtered off. Examination under the polarizing microscope showed it to be methylpicramide, with no indication of unchanged material. After one crystallisation from alcohol it had m. p. and mixed m. p. 115°.

(*b*) 2 : 4-Dinitrophenylmethylnitramine (0·57 g.) and 2 : 4-dinitrodimethylaniline (0·5 g.) were each dissolved in 10 c.c. of concentrated sulphuric acid, and the solutions mixed. After being kept overnight, the solution was poured into water, and the yellow precipitate filtered off. Microscopic examination, confirmed by fractional crystallisation from alcohol, showed the products to be methylpicramide and 2 : 4-dinitrodimethylaniline.

(*c*) A similar experiment, using *p*-nitromethylaniline and 2 : 4-dinitrophenylnitramine, yielded unchanged *p*-nitromethylaniline and methylpicramide.

Development of Purple Colour by Possible Tetryl Intermediates.—A small amount of substance was warmed on the water-bath with standard nitrating acid. 2 : 4-Dinitrodimethylaniline, 2 : 4-dinitromonomethylaniline, 2 : 4-dinitro-*N*-nitrosomonomethylaniline, and 2 : 4-dinitrophenylmethylnitramine gave a purple colour, but mono- and di-methylpicramide did not.

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THE UNIVERSITY, BRISTOL, 8.

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