347. *Nitramines and Nitramides. Part III.* The Formation of Nitric Acid by the Action of Sulphuric Acid.*

By C. Holstead and Alex. H. Lamberton.

Many nitramides have been found to give nitric acid on dissolution in sulphuric acid. With the noteworthy exception of cyclonite, nitramines give little, and often no, nitric acid under similar conditions. A condensation product has been isolated which indicates that nitramine, in association with formaldehyde, can play a synthetic role in concentrated sulphuric acid.

It has been known for many years that some *N*-nitro-compounds could act, in sulphuric acid, as nitrating agents. This has been demonstrated by the use of nitrourethane (Thiele, *Annalen*, 1897, **296**, 108), nitroguanidine (Davis and Abrams, *Proc. Amer. Acad. Arts Sci.*, 1926, **61**, 437; *Chem. Zentr.*, 1927, I, 2295), and nitrobiuret (Davis and Blanchard, *J. Amer. Chem. Soc.*, 1929, **51**, 1801). Denitration is also known to be possible in the case of compounds such as tetryl (Romburgh, *Rec. Trav. chim.*, 1886, **5**, 240; Jones and Willson, *J.*, 1930, 2277), and occurs, though very possibly without the actual liberation of nitric acid (Hughes and Jones, *J.*, 1950, 2678), in the Bamberger–Orton conversion of aromatic nitramines into *C*-nitro-anilines.

Little stress has hitherto been laid on these observations, and the reaction appears to be more general than had been supposed. We have added, under standard conditions, various *N*-nitro-compounds to acetanilide (1 molecule for each nitro-group potentially available) dissolved in the sulphuric acid, and have used the formation of *p*-nitroacetanilide as a measure of the nitric acid produced.

The compounds examined may, for convenience in discussion, be divided into three

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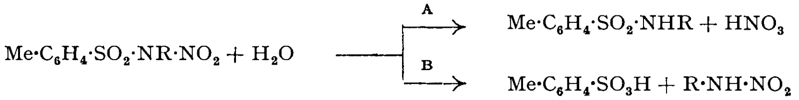
* *J.*, 1949, 1883, and 1951, 1282, are regarded as Parts I and II of this series.

groups. In the first group (Experimental, Table 1) we place the nitramides, both primary and secondary, and also the nitroguanidines. It is true that the zwitterionic nitroguanidines are not themselves nitramides, but we are here dealing with their salts [*e.g.*, $NO_2{\cdot}NH{\cdot}C(NH_2)_2^+$], and the amidinium portion $-C(NH_2)_2^+$ may be regarded as acylic in character. In the second group (Experimental, Table 3) we consider some simple secondary nitramines. They have been found, in many cases, to be stable under conditions which usually bring about the liberation of nitric acid from compounds in Group I; and, even under more drastic treatment, little, if any, nitric acid is formed. The third group (Experimental, Table 4) consists of derivatives of methylenediamine, and might be further sub-divided into the aminomethylnitramines ($R_2N{\cdot}CH_2{\cdot}NR'{\cdot}NO_2$) and the methylenepolynitramines ($NO_2{\cdot}NR{\cdot}CH_2{\cdot}NR{\cdot}NO_2$). The common feature of the compounds in the third group is that methylene fragments may become available for synthetic purposes. Nitric acid was also produced, though only in significant amounts when stronger sulphuric acid (99·7% in place of 95·2%, w/w) was used.

It can be seen from Table 1 (p. 1889) that nitroguanidine (2), ethylnitroguanidine (3), nitrourea (5), nitrourethane (6), and a range of secondary nitramides which can be regarded as structurally related to nitrourethane [7—12; all contain $-N(NO_2){\cdot}CO{\cdot}O-$] furnished nitric acid readily, and often provided a better yield of *p*-nitroacetanilide than potassium nitrate itself. The isolation of guanidine, urethane, and *N*-alkylurethanes suggests a simple denitration: it may be that the nitration process is reversible, though our qualitative evidence is not a strict proof. R. J. J. Simkins and G. Williams (personal communication) have shown, by quantitative measurements, that the conversion of the guanidinium ion into the nitroguanidinium ion is reversible. The yield of *p*-nitroacetanilide from the carbonic acid derivative, ethylenedinitrourea (tetrahydro-2-keto-1 : 3-dinitroglyoxaline) (13), showed that both nitro-groups were available. The acetyl compound examined (17) did not provide nitric acid, and was shown to give acetic acid on treatment with sulphuric acid alone.

The *N*-nitrosulphonamides (14, 15, and 16) gave some nitric acid, though the yield from (16) was small, and *p*-nitroacetanilide could not in this case be isolated by our normal technique. The formation of toluene-*p*-sulphonic acid suggested competitive modes of decomposition. If the overall reaction is formulated as a hydrolysis, these are

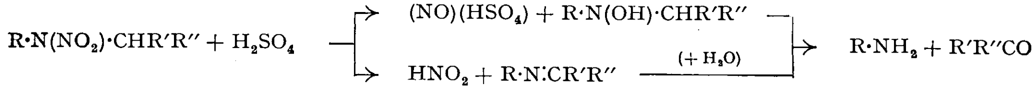


$$Me{\cdot}C_6H_4{\cdot}SO_2{\cdot}NR{\cdot}NO_2 + H_2O \quad \begin{array}{l} \xrightarrow{\text{A}} Me{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHR + HNO_3 \\ \xrightarrow{\text{B}} Me{\cdot}C_6H_4{\cdot}SO_3H + R{\cdot}NH{\cdot}NO_2 \end{array}$$

and it was found that the nitric acid formed by route A converted a considerable proportion of the sulphonic acid (route B) into *o*-nitrotoluene-*p*-sulphonic acid. Changing the strength of sulphuric acid from 95% to 100% (w/w) had very little influence on the outcome, though the change possibly favoured route A. It seemed unlikely, since we found no sign of the production of *o*-nitrotoluene-*p*-sulphonamides, that the nitric acid formed by partial decomposition converted any of the residual nitramide into an *N*-nitro-*o*-nitrotoluene-*p*-sulphonamide. Treatment of the *N*-nitrosulphonamides with sulphuric acid alone (Table 2) confirmed these results. Estimation of the total yield of the various products (p. 1891) suggested that the addition of acetanilide had no influence upon the routes of decomposition when (15) a sufficiency of the nitratable toluene-*p*-sulphonic acid was in any case formed: when this was not so (14), the addition of acetanilide slightly favoured the (reversible) route *A* through the removal of nitric acid.

The simple secondary nitramines (Table 3) did not, with the exception of di*cyclo*hexylnitramine (21), give any *p*-nitroacetanilide. In 95% sulphuric acid this was in part due to their stability (19*a*, 20*a*); but, even under conditions drastic enough to decompose all (or most) of the nitramine, no nitroacetanilide was obtained. The recovery of part of the acetanilide showed that, if it had been formed, nitric acid would have had the opportunity of nitrating the anilide: *p*-nitroacetanilide was found, in separate experiments, to be unaffected by sulphuric acid under the conditions used. We conclude that significant quantities of nitric acid cannot be formed by the decomposition of these nitramines.

Franchimont and his school made several vague references (*e.g.*, *Rec. Trav. chim.*, 1898, **17**, 287) to the action of sulphuric acid on secondary nitramines; and Backer (*Ahrens Sammlung*, 1912, **18**, 359) suggested the formation of either a hydroxylamine or a Schiff's base as intermediates in the ultimate production of an amine and a carbonyl compound:



$$R{\cdot}N(NO_2){\cdot}CHR'R'' + H_2SO_4 \rightarrow \begin{cases} (NO)(HSO_4) + R{\cdot}N(OH){\cdot}CHR'R'' \\ HNO_2 + R{\cdot}N{:}CR'R'' \xrightarrow{(+H_2O)} \end{cases} \rightarrow R{\cdot}NH_2 + R'R''CO$$

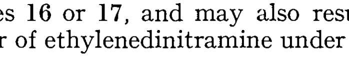
We have examined the products which resulted from the action of sulphuric acid alone (95·2% w/w) on di*cyclo*hexylnitramine and on dimethylnitramine. In the first case di*cyclo*hexylnitrosamine was precipitated on dilution with water: from the filtrate, which contained nitrous acid, *cyclo*hexylamine and *cyclo*hexanone were isolated as, respectively, the toluene-*p*-sulphonamide and the 2 : 4-dinitrophenylhydrazone. In all, 44% of the initial nitramine could be accounted for. The more stable dimethylnitramine has similarly been shown to yield at least some nitrous acid, formaldehyde, and methylamine. It appears that the suggestion of the early workers regarding the final products is correct, but we do not feel able, at present, to comment on the course of the reaction. The formation of the nitrosamine is incidental—since this product was found to be unaltered by further treatment with sulphuric acid—and is not unprecedented (Reverdin, *Chem. Zentr.*, 1910, I, 1020; 1911, I, 548; 1912, II, 110).

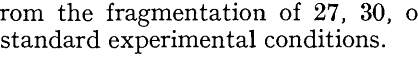
It was suggested to us, very pertinently, by Dr. J. P. Picard that denitration might occur only in those cases where the *N*-nitro-compound could be formed by direct nitration without the use of a chloride catalyst (Wright *et al.*, *Canad. J. Res.*, 1948, **26**, *B*, 89, 114). For this reason we examined two cyanonitramines (22 and 23) which can be prepared by the direct nitration of the parent (weakly basic) secondary amines. There was, however, no sign of denitration: instead, these cyanides were converted into the corresponding diamides.

Among the compounds listed in Table 4 only cyclonite (31) gave more than traces of *p*-nitroacetanilide on treatment with acetanilide in 95·2% sulphuric acid. The denitration reaction was obviously favoured by an increase in the sulphuric acid concentration: this effect was shown both in the case of aminomethylnitramines (28, 30) and cyclic polynitramines (31, 32, 33). The efficiency of cyclonite as a nitrating agent was more than twice that of any of the other compounds examined, and compares, at least in 99·7% acid, not too unfavourably with potassium nitrate itself. In all the compounds of this group gas was evolved on dissolution. This is known, at least in the case of cyclonite (E. Roberts, private communication), to be nitrous oxide; and a further portion of the initial nitrogen of cyclonite is converted into ammonium ions.

Condensation products were formed in most cases from acetanilide and fragments of the added nitramines. One such was di-*p*-acetamidophenylmethane (I) which is known (Ralston and McCorkle, *J. Amer. Chem. Soc.*, 1939, **61**, 1604) and results also from the addition of paraformaldehyde to acetanilide in sulphuric acid. The production of di-*p*-acetamidobenzylnitramine (II) indicates that nitramine (presumably closely associated with, and stabilised by, " formaldehyde ") can play a synthetic role in media as destructive as anhydrous sulphuric acid. The combined yield of compounds (I) and (II) in a crude condition was often considerable, but separation and purification was difficult. The best source of (II) was the linear polymethylenenitramine " B.S.X. " (29) and the structure of (II) has been proved by (*a*) hydrolysis to the nitramino-diamine (II; H in place of Ac), (*b*) reduction by zinc and acetic acid to (probably) the diacetyl-triamine (II; H in place of NO_2), and (*c*) reduction by tin and hydrochloric acid to the triamine (II; H in place of Ac and of NO_2).

(I)

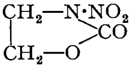
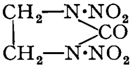




(II)

We have examined (since this nitramine is probably formed by sulphuric acid from the nitramides 16 or 17, and may also result from the fragmentation of 27, 30, or 32) the behaviour of ethylenedinitramine under our standard experimental conditions.

TABLE 1. *Action of nitroguanidines and of nitramides on acetanilide in sulphuric acid of* (*a*) 95·2%, *and* (*b*) 99·7%, *w*/*w*.

Ref. no.	*N*-Nitro-compound	Yield (%) of $NO_2·C_6H_4·NHAc$	Other products isolated
1*a*	KNO_3 (Standard)	72	—
1*b*	,, ,,	44—55	—
2*a*	$NH_2·C(NH)·NH·NO_2$	73	Guanidine (50%; note 1)
3*a*	$Et·NH·C(NH)·NH·NO_2$	76	—
3*b*	,,	44—51	—
4*a*	$NH_2·C(NH)·NH·CO·NH·NO_2$	66	—
4*b*	,,	41—53	—
5*a*	$NH_2·CO·NH·NO_2$	60	—
5*b*	,,	41—52	—
6*a*	$EtO_2C·NH·NO_2$	81	Urethane (33%; m. p. 45—48°; note 2)
6*b*	,,	43—55	—
7*a*	$EtO_2C·NMe·NO_2$	79	$EtO_2C·NHMe$ (39%; b. p. 67°/17 mm.; note 2)
8*a*	$EtO_2C·NPr^i·NO_2$	72	$EtO_2C·NHPr^i$ (76%; b. p. 71°/12 mm.; note 2)
9*a*	$EtO_2C·N(NO_2)·CH_2·CO_2Et$	78	—
10*a*	$EtO_2C·N(NO_2)·[CH_2]_2·N(NO_2)·CO_2Et$	70	—
10*b*	,,	41—55	—
11*a*	$MeO_2C·N(NO_2)·[CH_2]_3·N(NO_2)·CO_2Me$	78	—
12*a*		79	—
13*a*		76	—
14*a*	*p*-$C_6H_4Me·SO_2·NH·NO_2$	39	Ph·NHAc, $C_6H_4Me·SO_2·NH_2$ (33%; note 3), $C_6H_4Me·SO_3H$ (30%; note 4), and $C_6H_3Me(NO_2)·SO_3H$ (1%; note 4)
14*b*	,,	42	$C_6H_4Me·SO_2·NH_2$ (35%; note 3), $C_6H_4Me·SO_3H$ (15%; note 4), and $C_6H_3Me(NO_2)·SO_3H$ (9%; note 4)
15*a*	*p*-$C_6H_4Me·SO_2·NMe·NO_2$	15	Ph·NHAc, $C_6H_4Me·SO_2·NHMe$ (19%; note 3), $C_6H_4Me·SO_3H$ (50%; note 4), and $C_6H_3Me(NO_2)·SO_3H$ (5%; note 4)
15*b*	,,	18	$C_6H_4Me·SO_2·NHMe$ (24%; note 3), $C_6H_4Me·SO_3H$ (34%; note 4), and $C_6H_3Me(NO_2)·SO_3H$ (8%; note 4)
16*a*	$[·CH_2·N(NO_2)·SO_2·C_6H_4Me]_2$	1 (note 5)	Ph·NHAc, $C_6H_4Me·SO_3H$ (70%; note 4), and $C_6H_3Me(NO_2)·SO_3H$ (2%; note 4)
16*b*	,,	4 (note 5)	$C_6H_4Me·SO_3H$ (61%; note 4), and $C_6H_3Me(NO_2)·SO_3H$ (3%; note 4)
17*a*	$[·CH_2·N(NO_2)·COMe]_2$	Nil (note 5)	Ph·NHAc
17*b*	,,	Nil (note 5)	AcOH (71%; note 6)

Notes: (1) The initial filtrate was basified with barium hydroxide, the barium sulphate removed, and the excess of barium hydroxide precipitated as the carbonate by the passage of carbon dioxide. After filtration, nitric acid (2·5 ml.; 70%) was added, and the liquid evaporated to 10 ml. Cooling yielded guanidine as the nitrate, identified by m. p. and reconversion into nitroguanidine. (2) The initial filtrate was extracted with ether; when dried and distilled *in vacuo* the extract yielded a urethane, which was identified by m. p. or b. p., and by alkaline hydrolysis to yield a volatile base (ammonia, methylamine, or *iso*propylamine) which was converted into the corresponding toluene-*p*-sulphonamide. (3) The sulphonamides, which formed part of the initial precipitate, were separated by dissolution in aqueous sodium hydroxide, and were precipitated in a pure state on acidification. (4) The initial filtrate was treated with an aqueous solution of *S*-benzylthiuronium hydrochloride to precipitate the *S*-benzylthiuronium salts of toluene-*p*-sulphonic acid and *o*-nitrotoluene-*p*-sulphonic acid. The collected mixture of salts was analysed by (*a*) comparison of its m. p. with the m. p. diagram of mixtures of authentic materials, and (*b*) elemental (carbon) analysis. The mean value has been used in the calculation of yields. The following tabulation gives, successively, the reference number, the number of parts of the nitrated salt in 100 parts of the mixture as determined by methods (*a*) and (*b*), and the C, H values found for the mixture: 14*a*; 5, 4; C, 53·0; H, 5·8%. 14*b*; 39, 38; C, 50·9; H, 5·3%. 15*a*; 8, 9; C, 52·7; H, 5·6%. 15*b*; 22, 19; C, 52·2; H, 5·4%. 16*a*; 3, 3; C, 53·1; H, 5·6%. 16*b*; 6, 3; C, 53·1; H, 5·6% (Calc., for the salt of toluene-*p*-sulphonic acid, $C_{15}H_{18}O_3N_2S_2$: C, 53·3; H, 5·3%. Calc., for the salt of *o*-nitrotoluene-*p*-sulphonic acid, $C_{15}H_{17}O_5N_3S_2$: C, 47·0; H, 4·4%.) (5) *p*-Nitroacetanilide could not be isolated by the usual crystallisation from alcohol. Compound (16) gave the yields quoted on crystallisation from water, but no yield was thus obtained from (17). (6) After neutralisation with barium hydroxide acetic acid was precipitated from the initial filtrate as the *S*-benzylthiuronium salt. A comparable yield was obtained by treatment of the nitramide with sulphuric acid alone; hence the acetic acid cannot have come, in any quantity, from the acetanilide.

As was expected, from the known instability of primary nitramines towards acids, dissolution occurred with the immediate evolution of, presumably, nitrous oxide, and no *p*-nitroacetanilide was formed. The use of ethylenedinitramine provided an additional example of the behaviour, towards 95·2% w/w sulphuric acid, of a series of compounds of the general formula $NO_2{\cdot}NR{\cdot}CH_2{\cdot}CH_2{\cdot}NR{\cdot}NO_2$. These, if tabulated in the probable order of increasing acidity of ROH, are R = Me (19), H, $CMe_2{\cdot}CN$ (23), CO_2Et (10), $CO{\cdot}CH_3$ (17), and $SO_2{\cdot}C_6H_4Me$ (16). Of these only the urethane (10) and the sulphonamide (16) yielded nitric acid.

EXPERIMENTAL

Action of Nitramines and Nitramides on Acetanilide in Sulphuric Acid.—The *N*-nitro-compound (0·02 g.-equiv. of NO_2) was added, with stirring, in 20 minutes at 25°, to acetanilide (0·02 mole) freshly dissolved in sulphuric acid [20 ml. of (*a*) 95·2% or (*b*) 99·7%, w/w]. After a further 20 minutes at 25° the mixture was poured into ice and water (150 ml.). The precipitate was collected and crystallised from alcohol (50 ml.), for isolation of *p*-nitroacetanilide: a second crop was obtained by evaporation of the alcoholic mother-liquor to 10 ml. Yields quoted, in the *a* series, are the sum of these crops: m. p. >208°. In the *b* series the second crop was often impure, and the yields are then quoted as a range: *e.g.*, 44—55% indicates 44% of m. p. >208° and a second crop of 11%, m. p. >190° but <208°. Potassium nitrate was used, under identical conditions, as a standard for comparison (see Table 1).

TABLE 2. *Action of sulphuric acid on nitramides.*

Ref. no.	*N*-Nitro-compound	Concn. of H_2SO_4 (w/w)	Products isolated
14*c*	*p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}NO_2$	95·2%	$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ (37% of m. p. 136°), $C_6H_4Me{\cdot}SO_3H$ (2%; note 1), and $C_6H_3Me(NO_2){\cdot}SO_3H$ (41%; note 1)
14*d*	,,	99·7%	$C_6H_4Me{\cdot}SO_2{\cdot}NH_2$ (36% of m. p. 135°), and $C_6H_3Me(NO_2){\cdot}SO_3H$ (39%; note 1)
15*c*	*p*-$C_6H_4Me{\cdot}SO_2{\cdot}NMe{\cdot}NO_2$	95·2%	$C_6H_4Me{\cdot}SO_2{\cdot}NHMe$ (23% of m. p. 76°), $C_6H_4Me{\cdot}SO_3H$ (31%; note 1), and $C_6H_3Me(NO_2){\cdot}SO_3H$ (21%; note 1)
15*d*	,,	99·7%	$C_6H_4Me{\cdot}SO_2{\cdot}NHMe$ (28% of m. p. 76°), $C_6H_4Me{\cdot}SO_3H$ (14%; note 1), and $C_6H_3Me(NO_2){\cdot}SO_3H$ (31%; note 1)
16*c*	$[{\cdot}CH_2{\cdot}N(NO_2){\cdot}SO_2{\cdot}C_6H_4Me]_2$	95·2%	$C_6H_4Me{\cdot}SO_3H$ (62%; note 1), and $C_6H_3Me(NO_2){\cdot}SO_3H$ (9%; note 1)
16*d*	,,	99·7%	$C_6H_4Me{\cdot}SO_3H$ (58%; note 1), and $C_6H_3Me(NO_2){\cdot}SO_3H$ (20%; note 1)
17*c*	$[{\cdot}CH_2{\cdot}N(NO_2){\cdot}COMe]_2$	95·2%	AcOH (61%; note 2)

Notes: (1) The mixed *S*-benzylthiuronium salts of toluene-*p*-sulphonic acid and *o*-nitrotoluene-*p*-sulphonic acid were analysed as described in note 3 to Table 1; the results, reported in similar style, were: 14*c*; 98, 91; C, 47·6; H, 4·3%. 14*d*; 100, 100; C, 47·0; H, 4·5%. 15*c*; 48, 40; C, 50·8; H, 4·9%. 15*d*; 69, 76; C, 48·5; H, 4·9%. 16*c*; 15, 10; C, 52·7; H, 5·5%. 16*d*; 25, 31; C, 51·3; H, 5·4%. For calc. and required values, see note 4 to Table 1. (2) No precipitate was obtained on dilution of the solution of (17) in sulphuric acid with water, and extraction with methylene dichloride yielded no unchanged nitramide. After neutralisation with barium hydroxide, acetic acid was isolated as the *S*-benzylthiuronium salt of m. p. 150°.

Unchanged acetanilide was recovered from the majority of mixtures in which nitration to *p*-nitroacetanilide had not occurred. In the *a* series the acetanilide, if present in sufficient quantity, was precipitated on dilution with water, whilst in the *b* series it was necessary to extract it with ether. The isolation of acetanilide, when performed, is indicated in the tables, but the lack of indication for a particular experiment does not imply that residual acetanilide was proved to be absent.

Further details are given as notes after the individual tables. In these the expressions " initial ppt. " and " initial filtrate " refer to the precipitate, and the filtrate therefrom, which were obtained on pouring the sulphuric acid mixture into ice and water (150 ml.).

All products (apart from those which were analysed) were identified by m. p. and mixed m. p. with authentic materials. In some cases half-scale experiments were made, without any other alteration in procedure.

Stability of p-*Nitroacetanilide in Sulphuric Acid.*—*p*-Nitroacetanilide (3 g.) was added in

20 minutes at 25° to sulphuric acid (20 ml.). After a further 20 minutes at 25°, the residual *p*-nitroacetanilide was recovered by our standard procedure: recovery 86% and 67—79%, from 95·2% w/w and 99·7% w/w acid, respectively. After 16 hours at 25° in the 99·7% w/w acid, the recovery was 62—76%.

Treatment of Some Nitramides with Sulphuric Acid Alone.—The nitramides were treated with sulphuric acid under our standard conditions, but in the absence of acetanilide. Sulphonamides, when formed, were precipitated in a pure condition on dilution with water. Sulphonic acids, and acetic acid, were isolated as *S*-benzylthiuronium salts. Details are given in Table 2.

Balance-sheet of Materials in Experiments with N-*Nitrosulphonamides.*—Isolation of the products of decomposition could not be quantitative, since the sulphonamides and the *S*-benzylthiuronium salts are slightly water-soluble. We found, as a result of trial precipitations under our standard conditions, that the loss of toluene-*p*-sulphonamide was approximately 25% of the theoretically possible yield in experiments 14*a* and 14*b* (which involve two precipitations) and 16% in experiments 14*c* and 14*d*. The loss, for the less soluble *N*-methyltoluene-*p*-sulphonamide, was 11% in experiments 15*a* and 15*b*, and 7% in experiments 15*c* and 15*d*. Similarly, the probable losses of the *S*-benzylthiuronium salts of toluene-*p*-sulphonic acid and *o*-nitrotoluene-*p*-sulphonic acid were 8 and 6% respectively. By adding these figures to the percentage yields isolated (as quoted in Tables 1 and 2) we estimated the total yield of the various products. In experiments 14*a* to 14*d*, and 15*a* to 15*d*, this total of sulphonamide *plus* sulphonic acids was 100 ± 10% (average 99%), whilst the difference between the sulphonamide and the total of nitrated products (*o*-nitrotoluene-*p*-sulphonic acid and, if relevant, *crude* *p*-nitroacetanilide) was never more than 8% (average, sulphonamide 3% > total of nitrated materials). These figures enable us to say, with some confidence, that the routes A and B (p. 1887) are the only significant modes of decomposition.

With compound (16) the balance was less exact. We could account for about 85% of the initial material, and, in addition, a little ill-defined sulphonamide-like material could be isolated but not characterised. This was hardly surprising, since the total of nitric acid was low, and both nitramide groups must independently give rise to nitric acid if the pure disulphonamide is to be formed.

Separation of the S-*Benzylthiuronium Salts of Toluene*-p-*sulphonic Acid and* o-*Nitrotoluene*-p-*sulphonic Acid.*—The mixture of salts (*e.g.*, from experiment 15*c*) (0·4 g. of m. p. 161—164°) was decomposed by dissolution in 2N-sodium hydroxide (4 ml.). After a few minutes the solution was acidified with 2N-hydrochloric acid (5 ml.) and the liberated toluene-ω-thiol volatilised by boiling to a volume of 3 ml. Addition of barium chloride (4 ml. of M/4) to the cooled concentrate precipitated barium *o*-nitrotoluene-*p*-sulphonate, which was collected, dissolved in hot water, and reconverted, by the addition of *S*-benzylthiuronium hydrochloride and cooling, into the pure *S-benzylthiuronium* salt [0·06 g. of m. p. 163—164°, identical with material produced in experiment 14*d* (*q.v.* for analysis) or prepared from authentic *o*-nitrotoluene-*p*-sulphonic acid]. Treatment of the mother-liquor from the collection of barium *o*-nitrotoluene-*p*-sulphonate with *S*-benzylthiuronium hydrochloride gave a crude salt of toluene-*p*-sulphonic acid (0·06 g. of m. p. 175—177°; the pure salt has m. p. 181°) which still contained about 12% of the nitrated acid.

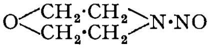
Treatment of Some Secondary Nitramines with Sulphuric Acid Alone.—(*a*) Di*cyclo*hexylnitramine was treated with sulphuric acid (95·2% w/w) under our standard conditions, but in the absence of acetanilide. The precipitate obtained on dilution was collected and crystallised from alcohol, to yield di*cyclo*hexylnitrosamine (13%; m. p. 102°). Half of the aqueous filtrate was basified with sodium hydroxide, and steam-distilled; from the distillate *cyclo*hexylamine was isolated in 10% yield as *N*-*cyclo*hexyltoluene-*p*-sulphonamide (m. p. 86°, as given by Hall and Turner, *J.*, 1945, 696). From the remaining half, *cyclo*hexanone was isolated (in 31% yield on basis 1 mole of nitramine ⟶ 1 mole of *cyclo*hexanone) as the 2 : 4-dinitrophenylhydrazone, m. p. 157°. *cyclo*Hexanone was characterised, additionally, by formation of the semicarbazone (m. p. 166°). In this, as in experiment 21*a*, the di*cyclo*hexylnitrosamine was of lower m. p. than the material (105°) obtained from experiment 21*b*, or synthetically. We believe that the impurity was unchanged di*cyclo*hexylnitramine. Re-treatment with sulphuric acid gave pure di*cyclo*hexylnitrosamine and showed, since the recovery was nearly quantitative, that the nitrosamine cannot be an intermediate in the formation of *cyclo*hexylamine and of *cyclo*hexanone.

(*b*) Similar treatment of dimethylnitramine gave dimethylamine (19%; determined by distillation into standard hydrochloric acid), identified by formation of *N*-methyltoluene-*p*-sulphonamide (m. p. 77°), and the 2 : 4-dinitrophenylhydrazone of formaldehyde (18%; m. p. 162°). In addition, 8% of the original nitramine could be recovered.

(*c*) Nitromorpholine was treated under our standard conditions with sulphuric acid alone (95·2%, w/w), and was recovered (79%) by extraction of the diluted aqueous acid with chloroform, and vacuum-distillation.

In all cases (*a*, *b*, and *c*) the diluted aqueous acid was found to contain nitrous acid by the sulphanilic acid–α-naphthylamine colour test.

TABLE 3. *Action of simple secondary nitramides on acetanilide in sulphuric acid of* (*a*) 95·2% *and* (*b*) 99·7%, *w/w.*

Ref. no.	*N*-Nitro-compound	Products isolated, and remarks
18*a*	$Me_2N{\cdot}NO_2$	Ph·NHAc, and initial nitramine (28%; note 1)
18*b* (1)	,,	,, (20%; note 1)
18*b* (2)	,,	Kept, after addition, for 15 hours at 25°; no nitramine recovered
19*a* (1)	$NMe(NO_2){\cdot}CH_2{\cdot}CH_2{\cdot}NMe(NO_2)$	Ph·NHAc, and initial nitramine (80%; note 2)
19*a* (2)	,,	Kept, after addition, for 1½ hours at 50°: Ph·NHAc, and initial nitramine (44%; note 3)
19*a* (3)	,,	Kept, after addition, for 70 hours at 25°: initial nitramine (38%; note 3)
19*b*	,,	Kept, after addition, for 15 hours at 25°; initial nitramine (39%; note 3)
20*a*	 $O{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}N{\cdot}NO_2$	Ph·NHAc; initial nitramine presumably unchanged (see action of sulphuric acid alone), but not isolated from filtrate
20*b* (1)	,,	Initial nitramine (44%; note 4)
20*b* (2)	,,	Kept, after addition, for 15 hours at 25°; no nitramine recovered
21*a*	$(C_6H_{11})_2N{\cdot}NO_2$	*p*-Nitroacetanilide (7%), and di*cyclo*hexylnitrosamine (10%; note 5)
21*b*	,,	*p*-Nitroacetanilide (11%), and di*cyclo*hexylnitrosamine (13%; note 5)
22*a*	$CN{\cdot}CH_2{\cdot}N(NO_2){\cdot}CH_2{\cdot}CN$	Ph·NHAc, and amide (14%; note 6)
23*a*	$[{\cdot}CH_2{\cdot}N(NO_2){\cdot}CMe_2{\cdot}CN]_2$	Ph·NHAc, and amide (66%; note 7)
24*b*	(*p*-NHAc·$C_6H_4{\cdot}CH_2)_2N{\cdot}NO_2$	Initial nitramine (57%; note 3)

Notes: (1) Dimethylnitramine was extracted from the initial filtrate with ether, and separated from acetanilide by sublimation. (2) Acetanilide was removed from the initial ppt. by cold alcohol leaving a residue of pure *NN'*-dimethylethylenedinitramine. (3) The initial ppt. consisted solely of unchanged nitramine. (4) No initial ppt. was obtained; the solution was extracted with chloroform, and pure nitromorpholine isolated by distillation *in vacuo*. (5) The initial ppt. was triturated with cold ether, and the insoluble *p*-nitroacetanilide worked up in the usual manner. The ethereal solution was evaporated, and the residue crystallised from aqueous alcohol, to yield di*cyclo*hexylnitrosamine. (6) After 3 days the initial filtrate deposited the diamide (14%; m. p. 223°), which crystallised from water in shining plates, m. p. 224° (decomp.) (Found: C, 27·6; H, 4·3; N, 31·5. Calc. for $C_4H_8O_4N_4$: C, 27·3; H, 4·4; N, 31·7%). Franchimont and Dubsky (*Rec. Trav. chim.*, 1916, **36**, 104) gave m. p. 218° (decomp.) for a crude specimen. (7) Acetanilide was removed from the initial ppt. by trituration with cold alcohol. The insoluble *NN'-di-*(2-*carbamylprop*-2-*yl*)*ethylenebisnitramine* (66%; m. p. 274°, decomp.) crystallised from water in prisms; m. p. 278° (decomp.) (Found: C, 37·8; H, 6·0; N, 25·8. $C_{10}H_{20}O_6N_6$ requires C, 37·5; H, 6·3; N, 26·2%).

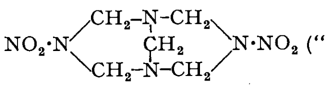
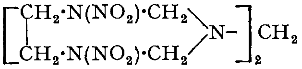
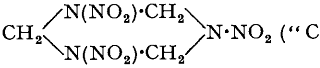
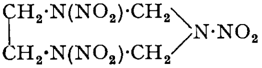
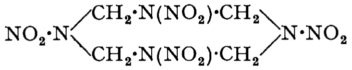
Di-p-*acetamidophenylmethane* (I).—Acetanilide (2·7 g.) was dissolved in concentrated sulphuric acid (20 ml.), and paraformaldehyde (0·1 g.) added portionwise at 25° in 20 minutes. After a further 20 minutes the mixture was poured into ice and water (150 ml.), and the resultant precipitate crystallised several times from alcohol, to yield di-*p*-acetamidophenylmethane (0·1 g.), m. p. 233° (Found: C, 72·2; H, 6·4; N, 9·8. Calc. for $C_{17}H_{18}O_2N_2$: C, 72·3; H, 6·4; N, 9·9%). Authentic material prepared from di-*p*-aminophenylmethane and acetic anhydride. M. p.s ranging from 227° to 236° have been reported (Ralston and McCorkle, *loc. cit.*).

Di-p-*acetamidobenzylnitramine* (II).—1 : 7-Diacetoxy-2 : 4 : 6-trinitro-2 : 4 : 6-triazaheptane ("B.S.X") (1 g.) was added portionwise in 20 minutes at 25° to acetanilide (2·7 g.) in concentrated sulphuric acid (20 ml.). After a further 30 minutes at 25° the mixture was poured into ice and water (150 ml.). The precipitate was collected and (without preliminary drying) crystallised twice from alcohol, to yield the *nitramine* as needles (0·6 g.), m. p. 236° (Found: C, 60·3; H, 5·8; N, 15·5. $C_{18}H_{20}O_4N_4$ requires C, 60·6; H, 5·6; N, 15·7%).

Di-p-*aminobenzylnitramine.*—Di-*p*-acetamidobenzylnitramine (0·5 g.) was heated under reflux for 1 hour with concentrated hydrochloric acid (5 ml.) and ethanol (5 ml.). The *dihydrochloride* of di-*p*-aminobenzylnitramine separated from the hot solution and recrystallised from concentrated hydrochloric acid as platelets (0·35 g.), decomp. when heated (no m. p.) (Found: C, 48·7; H, 5·2; N, 16·6; Cl, 20·9. $C_{14}H_{18}O_2N_4Cl_2$ requires C, 48·7; H, 5·2; N, 16·3; Cl, 20·6%). The salt was dissolved in water, and basified with sodium hydroxide. The precipitated *di*-p-*aminobenzylnitramine* crystallised from alcohol in colourless plates, m. p. 157°, becoming brown on exposure to the air [Found: C, 61·5; H, 5·7; N, 20·2%; *M* (Rast), 283. $C_{14}H_{16}O_2N_4$ requires C, 61·8; H, 5·9; N, 20·5%; *M*, 272].

Di-p-*acetamidobenzylamine*.—Di-*p*-acetamidobenzylnitramine (0·5 g.) was heated for 2·5 hours under reflux with glacial acetic acid (5 ml.) and zinc dust (1 g.). After cooling, the excess of zinc was removed, and the filtrate diluted with water, basified with sodium hydroxide, washed with ether, and extracted with chloroform. Evaporation of the chloroform yielded a glassy solid (m. p. 50—60°) which could not be purified, but which was converted into the *hydrochloride* (needles which charred on being heated) by crystallisation from 2N-hydrochloric acid (Found: C, 59·1; H, 6·7; N, 11·4; Cl, 9·5. $C_{18}H_{22}O_2N_3Cl$ requires C, 62·1; H, 6·3; N, 12·1; Cl, 10·2%). The smallness of the yield made full purification impossible.

TABLE 4. *Action of nitrated methylenediamines (aminomethylnitramines and polynitramines) on acetanilide in sulphuric acid of (a)* 95·2% *and (b)* 99·7% *w/w.*

Ref. no.	*N*-Nitro-compound	Yield (%) of $NO_2{\cdot}C_6H_4{\cdot}NHAc$	Other products isolated
25*a*	$NO_2{\cdot}NH{\cdot}CH_2{\cdot}NH{\cdot}NO_2$	nil	Compounds (I) (0·05 g.) and (II) (0·09 g.)
26*a*	$NO_2{\cdot}NAc{\cdot}CH_2{\cdot}NAc{\cdot}NO_2$	nil	Compounds (I) (0·1 g.) and (II) (0·05 g.)
27*a*	$\{O<[CH_2]_2>N{\cdot}CH_2{\cdot}N(NO_2){\cdot}CH_2{\cdot}\}_2$	nil	Ph·NHAc, and compound (I) (0·04 g.)
28*a*	 ("D.P.T.")	nil	Compound (II) (0·18 g.)
28*b*	„	13	—
29*a*	$AcO{\cdot}[CH_2{\cdot}N(NO_2)]_3{\cdot}CH_2{\cdot}OAc$ ("B.S.X.")	nil	Compound (II) (0·65 g.)
29*b*	„	nil	Compound (II) (0·2 g.)
30*a*		1	Ph·NHAc
30*b*	„	22	—
31*a*	 ("Cyclonite")	30	—
31*b*	„	45	—
32*a*	 ("Homocyclonite")	nil	Compounds (I) (0·05 g. and (II) (0·37 g.)
32*b*	„	14	—
33*a*	 ("H.M.X.")	1	Compound (II) (0·04 g.)
33*b*	„	18	Compound (II) (0·1 g.)

Note: The condensation products (I) and (II) were isolated (except in experiments 33*a*, 33*b*) by repeated fractional crystallisation of the initial ppt. from alcohol, in which (I) was the more soluble. In experiments 33*a* and *b* the initial ppt. was warmed with ethyl acetate: after cooling, compound (II) was collected and crystallised from alcohol. The ethyl acetate mother-liquor was evaporated, and *p*-nitroacetanilide isolated in the usual manner. The yields quoted in all cases are of the purified materials, m. p. 233° (I) and 236° (II).

Di-p-*aminobenzylamine*.—Di-*p*-acetamidobenzylnitramine (0·5 g.) was heated under reflux for 2·5 hours with tin (1 g.) and concentrated hydrochloric (10 ml.). The solution was then cooled, basified with aqueous sodium hydroxide, and extracted with ether. Evaporation yielded a brown oil, which was converted into the trihydrochloride (Strakosch, *Ber.*, 1873, **6**, 1060) by dissolution in alcohol and addition of a small volume of concentrated hydrochloric acid (Found, after crystallisation from concentrated hydrochloric acid: C, 49·7; H, 6·0; N, 12·4; Cl, 31·7. Calc. for $C_{14}H_{20}N_3Cl_3$: C, 49·9; H, 5·9; N, 12·4; Cl, 31·7%). The base was regenerated from the purified salt and, crystallised from *cyclo*hexane, had m. p. 105° and was identical in all respects with material synthesised from *p*-nitrobenzyl chloride by Strakosch's method (*loc. cit.*).

N-iso*Propylnitrourethane.*—*iso*Propylurethane (9 ml.) was added dropwise at −5° to nitric acid (15 ml.; 98%): the reaction readily became out of control if the temperature was allowed to rise. After the addition was complete the solution was poured at once into aqueous sodium carbonate (500 ml.) and extracted with ether. The extract yielded N-iso*propylnitrourethane* (10·5 g.; b. p. 84—85°/11 mm.) on drying and distillation (Found: C, 41·2; H, 7·1; N, 15·6%. $C_6H_{12}O_4N_2$ requires C, 40·9; H, 6·8; N, 15·9%). Curry and Mason (*J. Amer. Chem. Soc.*, 1951, **73**, 5045) have since reported b. p. 72°/7 mm.

Ethyl N-*Carbethoxynitraminoacetate.*—This compound was prepared by the method of Hantzsch and Metcalfe (*Ber.*, 1896, **29**, 1680), who did not attempt its purification. Extraction with ether, washing with aqueous sodium hydrogen carbonate, and distillation *in vacuo* yielded the pure *nitramide* as an oil, b. p. 148—149°/14 mm. (Found: C, 38·5; H, 5·8; N, 12·5. $C_7H_{12}O_6N_2$ requires C, 38·2; H, 5·5; N, 12·7%).

NN′-*Toluene*-p-*sulphonylethylenedinitramine.*—*NN*′-Toluene-*p*-sulphonylethylenediamine (Howard and Marckwald, *Ber.*, 1899, **32**, 2041) (6 g.) was added to nitric acid (26 ml.; 76%), and concentrated sulphuric acid (9 ml.) added dropwise at 0°. The mixture was poured into ice and water (250 ml.), and the resultant precipitate recrystallised from moist acetone, to yield NN′-*toluene*-p-*sulphonylethylenedinitramine* (4·5 g.) as needles, m. p. 176° (decomp.) (Found: C, 41·8; H, 4·0; N, 12·4; S, 13·9. $C_{16}H_{18}O_8N_4S_2$ requires C, 41·9; H, 3·9; N, 12·2; S, 14·0%).

2 : 7-*Dicyano*-2 : 7-*dimethyl*-3 : 6-*diazaoctane.*—Anhydrous ethylenediamine (3 ml.) was added dropwise in 20 minutes to acetone cyanohydrin (8·5 ml.), with cooling to keep the temperature below 60°. On cooling to 0° the liquid solidified. The solid was washed with ligroin (b. p. 40—60°), dissolved in *cyclo*hexane, freed from insoluble material by filtration, and allowed to crystallise by evaporation of the solvent. Recrystallisation from *cyclo*hexane yielded the dicyanodimethyldiazaoctane (6 g.; m. p. 56°). Jacobson (*J. Amer. Chem. Soc.*, 1945, **67**, 1996) gives m. p. 56°.

2 : 7-*Dicyano*-2 : 7-*dimethyl*-3 : 6-*dinitro*-3 : 6-*diazaoctane.*—2 : 7-Dicyano-2 : 7-dimethyl-3 : 6-diazaoctane (10 g.) was added with stirring to a mixture of acetic anhydride (48 ml.), acetyl chloride (1·5 ml.), and nitric acid (7·3 ml.; 100%) in 10 minutes at −50°. The dicyanodimethyldiazaoctane went into solution, and a fresh precipitate (probably a nitrate) soon separated. The reaction mixture was allowed to warm to 0° and, after 10 minutes at 0°, was set aside for 24 hours at 25° before being poured into ice and water (1400 ml.). The precipitate was collected, washed successively with water, alcohol, and ether, and crystallised from nitromethane (75 ml.), to yield the *dinitro*-compound as prismatic plates (6·8 g.), m. p. 212° (decomp.) (Found: C, 42·5; H, 5·8; N, 30·0. $C_{10}H_{16}O_4N_6$ requires C, 42·3; H, 5·6; N, 29·6%).

Other Compounds.—The remainder of the compounds used were furnished to us, or were prepared by known methods. Experiment numbers (from Tables 1, 2, or 3, and 4) and relevant references are: 3, McKay, *J. Amer. Chem. Soc.*, 1949, **71**, 1968; 5, Davis and Blanchard, *ibid.*, 1929, **51**, 1790; 6, Brian and Lamberton, *J.*, 1949, 1633; 7, Franchimont, *Rec. Trav. chim.*, 1894, **13**, 308; 10, Bachmann *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 3132; 11, Woodcock, *J.*, 1949, 1635; 12, Franchimont, *Rec. Trav. chim.*, 1902, **21**, 49; see Homeyer, *Chem. Abs.*, 1946, **40**, 4084, for initial amide; 13, as for 10; 14 and 15, Gillibrand and Lamberton, *J.*, 1949, 1883; 17, as for 10; 18, Wright *et al.*, *Canad. J. Res.*, 1948, **26**, *B*, 89; 19, Backer, *Rec. Trav. chim.*, 1912, **31**, 172; 20, 21, and 22, Wright *et al.*, *Canad. J. Res.*, 1948, **26**, *B*, 114; 25 and 26, as for 6; 27, as for 11; 28, Wright *et al.*, *Canad. J. Res.*, 1949, **27**, *B*, 218; 29, Bachman and Sheehan, *J. Amer. Chem. Soc.*, 1949, **71**, 1942; 30 and 32; Myers and Wright, *Canad. J. Res.*, 1949, **27**, *B*, 489.

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