[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ON 1,2- AND 1,4-ADDITION.[1] V. NITROGEN TETROXIDE AND TETRAMETHYLETHYLENE

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In an investigation on the addition of nitrogen tetroxide to tetramethylethylene, Demjanoff (1) obtained the crystalline, nitro-nitric ester, $(CH_3)_2C(ONO_2)C(NO_2)(CH_3)_2$ (I), a blue oil and, also, a bluish solid. The latter was considered to be the nitroso-nitric ester, $(CH_3)_2C(ONO_2)$-$C(NO)(CH_3)_2$ (II); because it was blue and, like the corresponding nitro ester I (2), it yielded 2-amino-2,3-dimethylbutanol-3 on reduction. On the other hand, Schmidt (3) concluded from his experimental results that the dinitrous ester, $(CH_3)_2C(ONO)C(ONO)(CH_3)_2$ (III), was formed as the main, and the dinitro compound, $(CH_3)_2C(NO_2)C(NO_2)(CH_3)_2$ (IV), as the minor product in the addition of nitrogen tetroxide, or "nitrous fumes," to the alkene in ether solution. The dinitro compound (IV) was obtained in a very low yield and was imperfectly investigated, but the structure of the dinitrous ester (III) was considered definitely established, as only ammonia was formed on reduction and, on hydrolysis with alkali, sodium nitrite appeared in practically quantitative yield. However, the other possible product, pinacol, was not isolated; indeed, no attempt was made to determine the nature of the organic product. In view of these divergent experimental results, Demjanoff and Ssidorenko (4) examined the action of "nitrous fumes" upon the alkene, and the results largely confirmed Demjanoff's earlier work. However, the bluish solid, previously believed to be nitroso-nitric ester (II), was completely purified and, in agreement with Schmidt, was identified, by reduction to tetramethylethylenediamine, as the dinitro compound (IV). Besides the dinitro compound (IV) and nitro-nitric ester (I), Demjanoff and Ssidorenko (4) isolated a third, crystalline solid (V), which was considered an inseparable mixture of nitro-nitric ester (I) and dinitro compound (IV). This conclusion was supported by analytical data, and by the formation of 2-amino-2,3-dimethylbutanol-3 and tetramethylethylenediamine on reduction. In this, as in the previous investigation, the formation of the dinitrous ester (III) could not be detected, yet Schmidt's result is generally accepted in the literature. Because of these conflicting statements, the action of nitrogen tetroxide on tetramethylethylene has been re-investigated.

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[1] Previous papers; (a) MICHAEL AND WEINER, *J. Am. Chem. Soc.*, **59**, 744 (1937); (b) MICHAEL AND CARLSON, *ibid.*, **59**, 843 (1937); (c) *J. Org. Chem.*, **4**, 169 (1939); **5**, 1 (1940).

Practically constant yields (19.5–22%) of 2,3-dinitro-2,3-dimethylbutane (IV) were obtained on treating tetramethylethylene with nitrogen tetroxide in ether solution (Table I, experiments 1–3), but the addition of gaseous tetroxide without solvent (experiments 4–5), or in petroleum ether solution (experiment 6), gave only small yields of the compound. Although a perfect separation of the components of the blue oil (experiments 4–6) could not be realized, our results show that the nitric ester of 2-nitro-2,3-dimethylbutanol-3 (I) constituted a considerable part of the reaction product. This nitric ester readily formed a double compound with the dinitro compound (IV) to yield a fairly soluble, crystalline substance; from a similar compound formed with diphenyldisulfide (experiment 4), the nitric ester component could be recovered only after the disulfide had been destructively oxidized. Since nitric ester (I) appeared in a relatively high yield only under the oxidizing action of the tetroxide (experiments 4–6), the disappearance of dinitro compound (IV) in these experiments may be attributed to a conversion to double compound (V). Nitrogen tetroxide appears to unite with tetramethylethylene under all experimental conditions to yield some dinitro compound (IV), but, although this product is relatively insoluble in organic solvents, isolation was only possible when the amount of nitric ester (I) present in the reaction mixture was insufficient for the complete conversion of the dinitro derivative into double compound (V).

Deep blue reaction products were formed (experiments 1–3 and 6) in the presence of and, also, in the absence of solvents (experiments 4–5), when the alkene was used in excess of the molecular proportion of the tetroxide. The blue substance, either the nitroso-nitric ester (II) or, for reasons mentioned below, the nitroso-nitro derivative $(CH_3)_2C(NO)C(NO_2)(CH_3)_2$, (VI), could not be isolated. While these products, like the nitrosyl chloride and bromide addition compounds of tetramethylethylene (5), are undoubtedly monomolecular, the nitrogen trioxide and tetroxide products, unlike the halogen compounds, failed to crystallize from the crude reaction product and a separation by distillation could not be realized. However, at a low temperature, the crude, and the distilled, blue oil solidified almost completely, but centrifuging the mixture at $-80°$ (experiment 6), or with an ether-petrol mixture as diluent (experiment 4), did not effect a complete separation of the solid from the oily product. The crude, and the distilled, blue oils were not acted upon by sodium methoxide or thiophenylate in the cold (experiments 1 and 6), but, in sealed tubes at 100°, mixtures of sodium nitrate and sodium nitrite were formed; with the mercaptide, a practically quantitative conversion to diphenyldisulfide occurred (experiments 4 and 6) and only a small amount of an oil appeared as a by-product. Although inert towards aniline, the nearly colorless oil in experiment 8, like the blue oils of other experiments, rapidly polymerized phenylisocyanate, but yielded no addition compound. The chemical nature of the oily products could not be established.

In experiments 7–9, tetramethylethylene, dissolved in ether, was treated with approximately three molecular equivalents of nitrogen tetroxide. The white, crystalline solid, which appeared at first in the blue reaction mixture, redissolved as the excess of the tetroxide was added and a pale green solution was formed. After removal of the solvent at reduced pressure, a practically colorless product was obtained, which solidified almost completely. However, separation of the small amount of adhering oil by filtration (experiment 7), or by centrifuging a suspension of the oily product in methyl alcohol at 0° (experiment 9), involved loss of considerable material; purification by steam-distillation was unsatisfactory because much of the product was decomposed. Analysis of the crystalline product (experiment 7) indicated that it was composed of 18% of the dinitro and 82% of the nitro-nitric ester derivative of tetramethylethane. Fractional crystallization did not change the properties of the solid, nor could it be separated into its components by sublimation at low pressure. On catalytic reduction, the sublimed product yielded ammonia, 2-amino-2,3-dimethylbutanol-3 and tetramethylethylenediamine. The diamine was precipitated practically quantitatively as the dihydrochloride on treating an acetic acid solution of the reduction product with hydrogen chloride; the yield indicated that the double compound (V) contained 22% of 2,3-dinitro-2,3-dimethylbutane, while the analytical data showed 18%. The semi-quantitative reduction and the analytical results are in fair agreement and establish the composition of V.

Under the oxidizing action of an excess of the tetroxide (experiments 7–9), product V appeared in a relatively high yield, but, under conditions tending to minimize the oxidative action, *viz.*, using ether as diluent and the alkene in excess, mainly the free dinitro compound was isolated (experiments 1–3). Although the tetroxide was used in an approximately equimolar proportion to the alkene in experiments 4 and 5, made without solvent, the yield of the double compound V was appreciable; it also constituted a large part of the reaction product formed in petroleum ether solution (experiment 6). These results lead to the conclusion that nitric ester (I), though formed under all conditions, appears only under oxidative conditions in amounts sufficient to combine with all of the dinitro compound (IV), which, probably, is mainly formed by direct addition of the tetroxide to the alkene. The reaction products in experiments 1–3 contained about 20% of the dinitro derivative (IV); the latter compound was completely incorporated into double compound (V) under the oxidative conditions of experiments 7–9. In view of the composition of V, these results indicate that the crude reaction product, when formed under sub-oxidative conditions, (experiments 1–3), contained at least 60% of nitroso-nitric ester (II), which, under favorable conditions, was oxidized to the corresponding nitro-nitric ester (I) and used in forming double compound (V) (experiments 4–9). Accordingly, the appearance of the dinitrous ester (III) as the main reaction product, as reported by Schmidt (3), is very improbable.

Immediately after preparation, 83% of the reaction product in experiment 4 was volatile at low pressure, but, 15–20 hours later, the distilled oil, which had been kept at −80°, yielded 57% of a very slowly volatile oil, from which nitric ester I was isolated in a yield of 46%. Refractionations of the reaction product in experiment 5 gave green, oily residues, from which nitric ester (I) and double compound (V) were isolated. These results indicate that the easily volatile, blue product, probably nitroso-nitric ester (II), or the nitroso-nitro compound (VI), underwent an autoxidation. The blue oil became discolored spontaneously, with apparent conversion of blue nitroso- to colorless, oxidized products, since corresponding reduction products could not be detected. However, the gradual separation of the more slowly from the easily volatile oils in experiments 4 and 5 may be attributed to an incomplete separation of these products by a single distillation, rather than to a slow chemical change of easily volatile into less volatile products. The isolated, pure products, even the high-melting dinitro compound (IV), sublimed readily at low pressure, but the liquid and the solid products have nearly the same vapor pressure and, therefore, a semi-quantitative separation of the reaction products by distillation was impossible. Separation of the products by crystallization entailed considerable loss of material. Accordingly, the relative yields of the primarily-formed reaction products could not be determined even approximately, and our experiments do not definitely establish the mode of formation of nitro-nitric ester (I).

Nitrogen tetroxide may act upon the easily oxidizable tetramethylethylene with formation of the corresponding alkylene oxide, which may unite with the tetroxide to yield nitro-nitric ester (I). However, the appearance of this ester, as was suggested by Demjanoff (4, 6), may also be attributed to oxidation of nitroso-nitric ester (II), which is probably formed primarily in the action of nitrogen tetroxide upon the alkene. Since nitro-nitric ester (I) appeared in a comparatively high yield in experiments 4–6, notwithstanding that the tetroxide and the alkene were used in approximately equivalent amounts, the primarily formed nitroso-nitric ester must undergo oxidation facilely and its conversion to the nitro-nitric ester undoubtedly proceeds concurrently with the addition of the tetroxide to the alkene.

Therefore, under the conditions of the above experiments, products formed from nitrogen trioxide[2] should appear; although such products could not be isolated, detection may have failed, owing to the difficulty of separating the components of the liquid reaction mixtures.

Like Demjanoff and Ssidorenko (4), whose experimental results have been fully confirmed, we found that a deep blue reaction product was formed when nitrogen tetroxide was added to the alkene in an equivalent, or a slightly lower, amount. Since Schmidt (3) did not notice a blue coloration, the appearance of dinitrous ester (III) in his product might be attributed to the use of the tetroxide in excess, but in experiments 7–9, in which nearly three molecular equivalents of the tetroxide was gradually added, a deep blue color appeared at first and was then only slowly discharged. From the nearly colorless solutions, no dinitrous ester (III) could be isolated and, with anhydrous nitrogen tetroxide, Schmidt's compound (III) could be obtained neither under mildly (experiments 1 and 2), nor strongly oxidative conditions (experiments 7–9); nor was this product isolated in experiment 3, in which the tetroxide was not dried with phosphoric anhydride. A trace of moisture did not noticeably alter the course of the reaction and under no conditions could the formation of this anomalous compound be confirmed.

EXPERIMENTAL

General procedure.—Tetramethylethylene dibromide was prepared by bubbling hydrogen bromide into pinacol hydrate (40 g.) at 0° until the solution fumed strongly. After 12–15 hours, the precipitated dibromide (27–29 g.) was filtered and washed with methyl alcohol; the combined filtrates from two preparations yielded 5.4 g. of an unidentified, lachrymatory bromine product[3] and 7 g. of pinacolone. The dibromide (40 g.) was reduced according to Thiele's (7) method and yielded 6–9 g. of tetramethylethylene, b.p. 73°.

Nitrogen tetroxide, prepared from anhydrous lead nitrate, was dried with phosphoric anhydride, condensed in a glass ampoule and then distilled into the reaction flask (experiments 4–6). In experiments 1–3, a weighed amount of the tetroxide was absorbed in ether, cooled to $-20°$, and the solution was added to the alkene; the tetroxide was not dried in experiment 3. The lead nitrate was decomposed slowly in experiments 7–9 and the evolved, cooled gas was passed directly into the alkene solution.

The solid reaction products were filtered, solvents removed from the filtrates and the liquid products were then treated as described in the footnotes to Table I. A mercury vapor pump was used for low pressure distillations.

Catalytic reduction.—The solid substance was dissolved in 25 cc. of glacial acetic

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[2] With tetramethylethylene, as with isopentene-2[1c] and isobutene, the trioxide should yield a nitroso-nitro addition compound, $(CH_3)_2C\ (NO_2)C(NO)(CH_3)_2$ (VI), which the oxidizing action of the tetroxide may convert to the dinitro compound (IV).

[3] KONDAKOFF [*J. pr. Chem.*, **54**, 429 (1896)], using hydrochloric acid, observed the formation of an analogous product.

TABLE I

EXPERIMENT NUMBER	1[a]	2	3[c]	4[d]	5[e]	6[f]	7[g]	8[h]	9[i]
Tetramethylethylene, g.	4	5.5	5.5	10	11	10	3	3	3
Nitrogen Tetroxide, g.	4	4.8	5.1	10.8	9.3	10.1	9	10.8	9
Solvent cc. Ether	25	30	30				10	30	30
Petrol						30			
Temp., °C.	−18	−20	−16	−10	−10	−14	−20	−18	−15
Time, mins.	30	10	20	70	90	40	20	17	30
Product, g. Solid (S)	1	1.8	1.1		0.02	0.1	3.8		
M.p., °C.	210–211	208–210	208–210			209–210	100–102		
Liquid (A)	6.9	7.3	8.2	20.1	20.2		1.9	6.7	6.1
Calc'd Yield, g.	7.6	9.2	9.7	20.7	17.8				
Dist. gave Blue dist. (B), g.				17.1		17.7			
Green, res. (C), g.				2.5		1.8			
% Dinitro compound	19.8	19.6	22						

In the footnotes, nitro-nitric ester (I), the dinitro- (IV) and the double compound (V) are represented, respectively, by D, E and F.

[a] Oil A, diluted with 5 cc. of petrol, deposited 0.5 g. of impure E, m.p. 195–205°. A suspension of E (0.2 g.) in 25 cc. of NaOH (0.1045 *N*) was heated in a sealed tube at 100° for 2 hours. The cooled mixture required 21.9 cc., and a control solution (25 cc.) 22.3 cc., of HCl (0.1169 *N*): the recovered E (0.2 g.) melted at 205–208°.

Two grams of A, treated with 0.3 g. of Na in 15 cc. of methyl alcohol gave no inorganic salt; solvent was distilled off *in vacuo*, the residue (0.7 g.) was acidified and yielded 0.01 g. of impure E, m.p. 200°, as the only identifiable product.

One gram of A, in 15 cc. of methyl alcohol containing platinum oxide catalyst, absorbed no hydrogen during 3 hours.

[c] Solid S was filtered off, the filtrate washed with water and sodium carbonate solution, dried and the solvent removed *in vacuo*. Oil A deposited 0.7 g. of blue solid (*1*), m.p. 160°: a portion of *1*, recrystallized from ether, gave E, m.p. 208–210°. A portion of crude *1*, exposed on tile for 12 hours, melted at 185–190°. The oil

separated from *1* was diluted with petrol and, during 24 hours, deposited 0.3 g. of E, which was crystallized from ether and then melted at 210–211°.

[d] Oil C solidified. The solid, recrystallized from ether at −80°, gave 1.1 g. of D, m.p. 88°: low pressure sublimation did not alter the m.p.

Oil B solidified at −80°. An ether solution of B, cooled to −80°, deposited a blue solid (*1*); solvent was distilled *in vacuo* from the decanted, ether solution. The residual oil (*2*) began to decompose at 2 mm. (bath-temperature 45°), but was rapidly cooled and a portion (3 g.), treated with a solution of 0.8 g. of Na in 25 cc. of methyl alcohol and 4 g. of thiophenol, gave 0.3 g. of inorganic salt (a mixture of sodium nitrate and nitrite; Found: Na, 31.6%) and 1.2 g. of diphenyldisulfide.

Solid *1* fused at about −50°; the blue liquid (7–8 g.) was distilled at low pressure and gave (*3*) 2.2 g. of blue distillate and (*4*) 4.6 g. of green, residual oil, which, crystallized from ether at −25°, gave 2.1 g. of D, m.p. 87°. Solvent was distilled from the filtrate and the residue, crystallized from methyl alcohol at −20°, gave D, m.p. 87°. When sublimed at low pressure, D melted at 88–89°. *Anal.* Calc'd for $C_6H_{12}N_2O_6$: C, 37.5; H, 6.3; N, 14.58. Found: C, 37.73; H, 6.07; N, 14.1. Mol. wt.: Calc'd: 192. Found: 179.

Two grams of D and a hot methyl alcohol solution of 1.4 g. of sodium thiophenylate gave no inorganic salt; solvent was distilled, the residue was extracted with ether and the extract yielded (*5*) 1.5 g. of a double compound of nitric ester (I) and diphenyldisulfide, m.p. 64–65°, which, sublimed at low pressure, melted at 64–65°. A portion of *5* (0.5 g.) was treated with 0.5 g. of chromic anhydride in 15 cc. of hot glacial acetic acid; the solution, poured into water, yielded a solid, which was sublimed and gave 0.3 g. of D, m.p. 88–89°.

[e] Oil A deposited no solid during 24 hours. At low pressure, A gave (*1*) a blue distillate and (*2*) 5.6 g. of greenish, residual oil. Crystallized from methyl alcohol at −80°, *2* gave 2 g. of a solid, from which, by low pressure sublimation, 1 g. of F, m.p. 100–103°, and 1 g. of a mixture of D and F, m.p. 90–95°, were obtained.

Oil *1*, distilled at low pressure, gave: (*3*) 5.2 g. of blue distillate and (*4*) 3.6 g. of greenish, residual oil, which solidified partially at −80° and yielded (*5*) 1.5 g. of a solid. On fractional sublimation, *5* gave (*6*) 0.8 g. of D, m.p. 88–89° and (*7*) 0.7 g. of impure D, m.p. 85–87°. Combined *6* and *7*, after resublimation, gave 1.2 g. of D, m.p. 86–87°, which was used for catalytic reduction (experiment 2, Table II). Refractionation of *3* gave (*8*) 1.4 g. of blue distillate and (*9*) 1.7 g. of residual oil, from which, by crystallization at −80° and sublimation of the crude solid at low pressure, 0.6 g. of impure D, m.p. 80–85°, was isolated.

[f] Solid S was filtered off, solvent distilled *in vacuo* from the filtrate and the residual oil distilled at low pressure (bath-temperature 20°). Oil C solidified; the product D was crystallized from ether at −25° and then sublimed at low pressure, m.p. 88–89°.

Oil B could not be separated into its components by distillation; the liquid (15.7 g.), diluted with 5 cc. of ether and cooled to −80°, deposited (*1*) 12.6 g. of a blue solid, which was separated by centrifuging at −80°. Solid *1* melted (at about −50°) to a blue oil (*2*), which, during 36 hours, deposited 1 g. of impure D, m.p. 75–77°; the solid was pressed on tile and then melted at 83–84°.

Three grams of *2* and a solution of 0.4 g. of sodium and 1.9 g. of thiophenol in 25 cc. of methyl alcohol, heated for 1 hour at 100°, gave 1.3 g. of inorganic salt (a mixture of sodium nitrate and nitrite, Found: Na, 29.2%) and 2 g. of oil, which yielded 1.6 g. of diphenyldisulfide.

[g] Crude S, recrystallized from an ether-petrol mixture, gave 3.5 g. of F, m.p. 100–102°. *Anal.* Found: C, 37.99, 38.34, 38.02; H, 5.58, 7.02, 6.04. Oil A solidified, but could not be purified. A solution of 0.5 g. of F and 0.6 g. of sodium in 25 cc.

of methyl alcohol was boiled, solvent was distilled from the clear solution, the residue was extracted with ether and from the extract 0.4 g. of unchanged F, m.p. 100–101°, was recovered.

[h] After 24 hours, the reaction mixture was washed with water, dried and the solvent distilled *in vacuo*. Oil A distilled very slowly at low pressure. A portion of A (4.1 g.) was steam-distilled; the volatilized oil (1.7 g.) and 2 g. of aniline gave no solid product.

[i] After 24 hours, the green, ether solution of the reaction product was poured into water, washed with sodium carbonate solution, dried and the solvent distilled *in vacuo*. Oil A solidified, but most of the solid fused in an attempt to separate oily product by filtration; the filtrate was solidified and the oil separated by centrifuging at 0°. The combined, isolated solids were recrystallized from methyl alcohol at 0°; the mixture, centrifuged at 0°, gave 1.8 g. of F, m.p. 104–105°.

TABLE II

EXPERIMENT	PRODUCT REDUCED		H_2 ABSORBED		PRODUCTS g.		
		g.	Cc.	Min.	NH_4Cl	Diamine di-HCl	Syrupy hydrochloride
1[a]	E	2.8	2155	2895		2.4	
2[b]	D	1.2	1005	2595	0.25		
3[c]	F	2.5	2055	3935			1.9

Letters D, E and F designate the same compounds as in Table I.

[a] After removal of the dihydrochloride, less than 0.1 g. of oily product was isolated from the acetic acid solution. A portion of the dihydrochloride (0.5 g.) and 1 g. of *p*-nitrobenzoyl chloride gave 1 g. of di-nitrobenzoate of tetramethylethylenediamine, m.p. 213–214°. *Anal.* Calc'd for $C_{20}H_{22}N_4O_6$: C, 58.00; H, 5.25; N, 13.55. Found: C, 57.93; H, 5.22; N, 13.81.

[b] The weight of the syrupy hydrochloride was not determined; the syrup and 1.2 g. of *p*-nitrobenzoyl chloride gave 0.2 g. of *p*-nitrobenzamide and an oil, from which 0.7 g. of the *p*-nitrobenzoate of 2-amino-2,3-dimethylbutanol-3, m.p. 137°, was isolated. After crystallization from benzene, the nitrobenzoate melted at 139°. *Anal.* Calc'd for $C_{13}H_{18}N_2O_4$: C, 58.6; H, 6.77; N, 10.55. Found: C, 58.75; H, 6.63; N, 10.74.

[c] The precipitated hydrochlorides (*1*) (0.9 g.) and 3.1 g. of *p*-nitrobenzoyl chloride gave 1 g. of impure di-*p*-nitrobenzoate of tetramethylethylenediamine, m.p. 203–210°, which, crystallized from benzene, gave (*2*) 0.6 g. of pure dinitrobenzoate, m.p. 211–212°, and (*3*) 0.4 g. of slightly impure product, m.p. 210°: accordingly, *1* contained 0.4 g. of ammonium chloride.

The syrupy hydrochloride (1.9 g.), which was isolated from the acetic acid solution of the reduction product, gave, with 2.5 g. of *p*-nitrobenzoyl chloride, 1 g. of solid (*4*) and 1.8 g. of oil (*5*), which, diluted with ether, deposited 0.9 g. of solid (*6*), m.p. 130°. Fractional crystallization of *4* gave 0.1 g. of *p*-nitrobenzamide, m.p. 198°, and (*7*) 0.7 g. of solid, m.p. 130°. Two forms of crystals were present in *6* and *7*, which could not be separated by crystallization. After two extractions with hot water and crystallization of the insoluble product from benzene, the combined solids (*6* and *7*) gave 0.6 g. of pure *p*-nitrobenzoate of 2-amino-2,3-dimethylbutanol-3, m.p. 139°, and 0.3 g. of impure product, m.p. 130–133°. The aqueous extracts yielded 0.2 g. of slightly impure nitrobenzoate of the amino alcohol, m.p. 136–137°.

acid (15 cc. of acid used in 2) and reduced in the usual manner, using platinum oxide catalyst and hydrogen slightly above atmospheric pressure. Catalyst was removed by filtration, hydrogen chloride bubbled into the filtrate and the precipitate was separated by filtration. The solvent was distilled *in vacuo* and the residue treated as described in the footnotes to Table II.

SUMMARY

1. The action of nitrogen tetroxide on tetramethylethylene has been examined under varied experimental conditions.

2. Practically constant yields (19.6–22%) of 2,3-dinitro-2,3-dimethylbutane are formed in ether solution; addition of gaseous tetroxide to the alkene without solvent, or in petroleum ether solution, gave only low yields of the dinitro compound.

3. The nitric ester of 2-nitro-2,3-dimethylbutanol-3 appears to be formed in variable amounts under all the examined, experimental conditions. In the absence of solvent and under strong oxidative conditions, the yield of the nitric ester is considerable. The nitric ester readily unites with 2,3-dinitro-2,3-dimethylbutane to form a double compound. Under the oxidizing action of an excess of the tetroxide, all of the dinitro compound is incorporated into this double compound. Accordingly, isolation of the dinitro compound is realized only under conditions tending to depress the oxidizing action of the tetroxide and the yield of the nitro-nitric ester. The composition of the double compound was deduced from the analytical data and from the relative amounts of the basic products obtained by catalytic reduction; *viz.*, ammonia, 2-amino-2,3-dimethylbutanol-3 and tetramethylethylenediamine.

4. The formation of the nitric ester of 2-nitro-2,3-dimethylbutanol-3 is discussed. The possibility is suggested that nitrogen tetroxide may oxidize tetramethylethylene to the corresponding oxide and then act upon the latter to yield the nitro-nitric ester. However, it is more probable that the nitro-nitric ester is formed by oxidation of the corresponding nitroso-nitric ester, which probably is formed primarily by direct addition of the tetroxide to the alkene.

5. With the alkene in excess and ether as diluent, 2,3-dinitro-2,3-dimethylbutane was obtained in yields of about 20%. Under the oxidizing action of excess tetroxide, all of the dinitro derivative appeared combined, as a double compound, with the nitric ester of 2-nitro-2,3-dimethylbutanol-3. These results, and the composition of the double compounds, indicate that the crude reaction product, formed with the reactants in approximately equivalent molecular amounts, consisted mainly of the dinitro derivative and the nitric ester of 2-nitroso-2,3-dimethylbutanol-3 and that the latter ester, under the oxidizing action of the tetroxide, was converted to the corresponding nitro-nitric ester, which combined with the dinitro derivative to the double compound.

6. Our results confirm those of Demjanoff and Ssidorenko. In agreement, the appearance of Schmidt's dinitrous ester could not be observed; until the precise conditions leading to the formation of this product are established, it should be omitted from the list of known organic compounds.

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