[Contribution from the Chemical Laboratory of Harvard University]

ON 1,2 AND 1,4 ADDITION[1]. III. NITROGEN TRIOXIDE AND TRIMETHYLETHYLENE

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In 1878, Lunge[2] showed that arsenous oxide and nitric acid of density 1.35 gave a gas containing nitrogen monoxide and dioxide in approximately equimolecular amounts, and that a more concentrated acid, in proportion to the density, gave nitrogen dioxide in excess. The significance of these results, however, has not been generally recognized in organic research[3]. In some of the researches on the "addition of nitrogen trioxide", the "nitrous fumes" were generated from the concentrated acid; in these investigations, the reaction mixtures contained a relatively large proportion of products derived from nitrogen tetroxide and were, therefore, only partially representative of the reactions of the trioxide. Extensive studies have been made on the addition of the higher oxides of nitrogen to alkenes, but the conflicting conclusions set forth in the literature, especially concerning the addition of the trioxide, attest to an imperfect understanding of the complex reactions.

Wallach[4] showed that trimethylethylene in acetic acid solution reacted with "nitrous fumes" from "concentrated" nitric acid to give the maximum yield (50%) of the so-called trimethylethylene nitrosate, subsequently shown to be the dimeric nitric ester of 2-methyl-3-nitrosobutanol-2[5], $[(CH_3)_2C(ONO_2)CH(NO)CH_3]_2$(I), and that with diluted acid lower yields

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[1] For previous papers, see: (*a*) Michael and Weiner, *J. Am. Chem. Soc.*, **59**, 744 (1937); (*b*) Michael and Carlson, *ibid.*, **59**, 843 (1937).

[2] (*a*) Lunge, *Ber.*, **11**, 1641 (1878). (*b*) For a complete resumé of the literature on this subject see, Gmelin, Handbuch, 8th ed. (1936), Syst. no. 4, 739.

[3] Wieland and Blümich [*Ann.*, **424**, 75 (1921)] showed that stilbene and "nitrous fumes" from concentrated nitric acid yielded a mixture of the nitroso-nitro, and the dinitro addition product, while the first compound was obtained almost exclusively with fumes from a diluted acid.

[4] Wallach, *Ann.*, **241**, 292 (1887).

[5] Schmidt, *Ber.*, **35**, 2336 (1902). Instead of the trivial names nitrosite and nitrosate, chemically correct terms are used. Even more irrelevant is the designation "pseudonitrosite", advanced by Wieland [*Ann.*, **328**, 156 (1903)] for nitroso-nitroxyl addition products to ethylene derivatives.

were produced. On the other hand, according to Schmidt[6], the moist gas generated from concentrated nitric acid (density 1.43) reacted with trimethylethylene in cold ether solution to form, primarily, a blue, oily product, which was assumed to be mainly the nitrous ester of 2-methyl-3-nitrosobutanol-2, $(CH_3)_2C(ONO)CH(NO)CH_3$(II); chiefly, because of its color and the gradual deposition of a crystalline compound, which was assumed to be the dimeric form of II, with a structure analogous to that of the nitric ester (I). The crude product decomposed on distillation, and the composition of the oil could not be ascertained definitely, yet Schmidt concluded that the primary reaction product consisted mainly of II and a small amount of I, which was assumed to be formed by oxidation of II. Although this conclusion is generally accepted in the literature, our results with trimethylethylene and nitrogen tetroxide[1b] show that, with addenda of such protean chemical properties as the higher oxides of nitrogen, the addition reactions are complex. We have, therefore, re-examined the reaction between trimethylethylene and "nitrous fumes", in order to determine the structure and the relative yields of the reaction products and to correlate the proportions of these products with the composition of the gases generated from arsenous oxide and nitric acid of varied concentration.

In our attempts to duplicate Schmidt's experiments, as far as is possible from the indefinite descriptions, we passed the moist gas generated from technical arsenous oxide and nitric acid (density 1.43 at 20°) into cooled ether solutions of trimethylethylene (experiments 1 and 2, Table I), but we obtained, instead of the polymerized nitrous ester (II), the corresponding, dimeric nitric ester, in amounts representing 1 per cent. and 0.8 per cent., respectively, of the reaction products; the main product, a greenish-blue oil, deposited no solid during two weeks. In Schmidt's and in these experiments the air in the apparatus was not removed; the oxygen, available for conversion of nitrogen trioxide to tetroxide, with consequent formation of organic products derived from the latter oxide, corresponded, in our experiments, to a maximum yield of tetroxide derivatives amounting to only 10–15 per cent. of the isolated reaction product, whereas the actual yield of tetroxide derivatives was much higher, as subsequent experiments showed. In an atmosphere of nitrogen, the moist gas, generated from nitric acid of density 1.43, acted upon trimethylethylene without solvent, to yield (experiment 4) 40.5 per cent. of the nitric ester (I); with acid of density 1.30, the yield decreased to 6.6 per cent. (experiment 5); yet 1 per cent. of the bisnitrate was formed with acid so dilute (density 1.23) that the "nitrous fumes" contained an excess of the monoxide, manifested by a continuous evolution from the reaction mixture (experi-

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[6] SCHMIDT, *Ber.*, **35**, 2323 (1902).

ment 6). These results lead to the conclusion that "nitrous fumes", even in the absence of atmospheric oxygen, yield derivatives of nitrogen tetroxide.

In previous experiments[1b], it was found that the dimeric nitrate (I), produced by the action of nitrogen tetroxide upon trimethylethylene without solvent, represented about 45 per cent. of the reaction product, and that an average yield of 33 per cent. was formed in petrol solution. Assuming that the bis-nitrate isolated in experiments 5 and 6 represents, similarly, 45 per cent. of the total product derived from nitrogen tetroxide, derivatives of the latter oxide constitute 14.5 per cent. and 1.4 per cent. of the respective reaction products. Whereas these values appear to be in accord with the chemical behavior of nitrogen trioxide, the estimated concentration of tetroxide derivatives, 90 per cent. and 57.5 per cent., respectively, in experiments 4 and 27 (Table IV), the former without and

TABLE I

REACTION OF "NITROUS FUMES" WITH TRIMETHYLETHYLENE

			Expt. No.	1	2	3	4	5	6
Trimethylethylene, g.				20	20	20	10	10	15
HNO_3, $d^{20°}$				1.433	1.431	1.41	1.431	1.302	1.225
Atmosphere				Air	Air	Air	Nitrogen	Nitrogen	Nitrogen
Temp., °C.				3–5	5–8	−10	0–10	0–5	0–5
Time, mins.				300	60	150	45	75	90
Products			Solid (A), g.	0.3	0.3	0.8	5.5	0.6	0.05
	Liquid		Total, g.	29.5	35.8	32.5	9.3	8.6	7.6
		gave	(A), g.	0	0	0.7	0.5	0	0
			(B), g.	0	0	0	0	0.7	0.6
			(a) Blue Filtrate, g.	29.5	35.8	28.2	3.3	7.8	6.7
% (A)				1.0	0.8	4.5	40.5	6.6	0.6
% (B)								7.6	7.8

Technical arsenous oxide (120 g.), 80 cc. of nitric acid and 60 cc. of ether were used in experiments 1–3; in 4–6, no solvent was used, and the gaseous reactant was generated from 60 g. of arsenous oxide and 40 cc. of the acid. Filtrate (*a*) gradually turned green, but deposited no solid (experiments 1, 2, and 4); the oil in experiment 3 distilled at low pressure to give 13.3 g. of blue distillate and 14.6 g. of green, residual oil; neither product was identified. The blue filtrate (*a*) (experiment 5) gave: (*1*) 2.7 g. of blue distillate, and (*2*) 5.2 g. of green, residual oil (molecular weight in freezing benzene, 235). On refractionation at 2 mm., fraction (*1*) gave a blue distillate (yield about 2 g.; n_D^{20} 1.4430; *Anal.* Found: C, 49.39; H, 7.41) and about 0.5 g. of greenish-blue, residual oil, n_D^{20} 1.4535. The blue distillate appeared to be identical with the corresponding oils isolated from the products prepared in ether solution (see Table III). Letter A designates $[(CH_3)_2C(ONO_2)CH(NO)CH_3]_2$ and B represents $[(CH_3)_2C(NO_2)CH(NO)CH_3]_2$.

the latter with petrol as solvent, cannot be reconciled with Lunge's analytical data[2a]. An entirely satisfactory explanation for these anomalies does not present itself. However, the course of reaction with nitrogen tetroxide varied greatly with the solvent[1b], and a similar "solvent effect" is not unlikely in reactions with nitrogen trioxide. Furthermore, the "trioxide" is largely dissociated, except at low temperature[2b] and, since the $-NO_2$ residue has a strong, but the $-NO$ residue a weaker, affinity for the unsaturated carbons of an alkene, loss of nitric oxide from the reaction mixture, with a preferential formation of a nitrogen tetroxide product, is not improbable. A gas mixture of anhydrous nitrogen tetroxide and the monoxide, with the latter in large excess, acted upon trimethylethylene, in ether solution at −25°, to yield an oil from which no solid product separated; at −80° in ether solution, a low (4.3 per cent.), and in petroleum ether a higher (the actual value cannot be stated because the filtered, liquid product decomposed vigorously), yield of nitrate (I) was obtained by treating trimethylethylene with the blue liquid formed by saturating nitrogen tetroxide with the monoxide at −80°. Whereas the solid product in these experiments was derived from nitrogen tetroxide, in experiments 5 and 6, with gases of approximately the composition of nitrogen trioxide[2a], a crystalline solid, undoubtedly identical with Schmidt's "bis-trimethylethylene-nitrosite", was obtained in low yields, 7.6 per cent. and 7.8 per cent., respectively. However, the product, contrary to Schmidt, is not the dimeric form of the nitroso-nitrite (II), but it is the dimeric nitroso-nitro derivative of trimethylethane, $[(CH_3)_2C(NO_2)CH(NO)CH_3]_2$(III), yielding the corresponding, monomeric diamine when reduced catalytically. Because neither "nitrous fumes", though containing an excess of the monoxide, nor the relatively pure, liquid "nitrogen trioxide" acted upon trimethylethylene to yield compound III, and the latter appeared in only low yields in experiments 5 and 6, notwithstanding that the experimental conditions were seemingly favorable for the formation of the derivative of nitrogen trioxide, the formation of III as the main product, under the conditions of Schmidt's experiments and with acid of density 1.43, is inexplicable.

From the results of thirty-five experiments, made under controlled conditions, a correlation between the yields of the reaction products and the experimental conditions is not discernible. The total product in experiment 11 (Table II) was 1.7 times that of experiment 10, and more than twice that of experiment 12, in which the reaction time was longer and the density of the acid only slightly less than in experiments 10 and 11. The results of the grouped experiments 2–4, 9–11, and 15–16 (Tables I and II) do not accord with the experimental conditions, and in the paired experiments 1–2, 7–8, 17–18, and 20–21 (Tables I, II, and IV), the yields of product are actually in an inverse order with respect to the time of reaction. The results obtained with moist "nitrous fumes" are no more consistent in the absence of than in the presence of air and, although almost identical yields of total product appeared in three experiments (24–26, Table IV), made with dried gas in an atmosphere of nitrogen, comparison with the result of experiment 23, made in the presence of air, shows that even under anhydrous conditions results differed widely. Equally discordant were the yields of the solid reaction products. At −10° (experiment 3, Table I), the product yielded 4.5 per cent. of the dimeric nitrate (I), but, in experiments 7 and 8 (Table II), the dimeric nitroso-nitro compound (III) separated in yields of 9.4 per cent. and 3.4 per cent., respectively, from the blue oils formed at 4° and 7°. These wide divergencies in the results of experiments 7–8 may depend, not only upon slight changes in experimental conditions, but, also, upon uncontrollable variations in the composition of the gaseous reactant. With nitric acid yielding nitrogen monoxide and dioxide in nearly the same quantity, a slight change in the concentration of the acid may alter the composition of the evolved gas materially, whereas a corresponding change, with an acid yielding a large excess of one of the oxides, may be comparatively slight. However, even with acids (density 1.242–1.312) yielding an excess of nitric oxide[2a], the results were not consistent, and the anomalous behavior of the arsenous oxide and nitric acid mixtures extends to acids of density varying from 1.242–1.433[7].

The moist gas, generated with nitric acid of density 1.30–1.312 (experiments 9–16, Table II), acted upon trimethylethylene in ether solution to form products yielding 8.6–17.4 per cent. of the dimeric nitroso-nitro compound (III). The best yield (17.4 per cent.) appeared in experiment 10, in which the product, immediately after preparation, was separated by distillation at low pressure into a slightly volatile green, and an easily volatile blue, oil from which the dimeric compound separated.

[7] Although Schmidt, and other early investigators, reported no difficulty in reproducing results with "nitrous fumes", Klemenc and co-workers [*Z. anorg. Chem.*, **115**, 131 (1921); **141**, 239 (1925)] found that the rate of oxidation of arsenous oxide by nitric acid varied, even under rigidly controlled conditions. Smith and Miller [*J. Ind. and Eng. Chem.*, **16**, 1168 (1924)] found that mercury, depending upon the concentration, promoted or inhibited the oxidation, yet, with respect to other varied and controlled factors, the experimental results could not be correlated and, although Ashenasy and Elöd [*Z. anorg. Chem.*, **162**, 161 (1927)] have shown that the rate of oxidation is dependent to a great extent upon the rate of solution of the arsenous acid, important factors which strongly influence the oxidation process remain unknown. In our experiments, the nitric acid and arsenous oxide mixtures were heated under identical conditions, yet the rate of formation of the "nitrous fumes" differed greatly, as was manifested by the formation, under seemingly comparable conditions, of variable yields of the organic products.

TABLE II

REACTION OF "NITROUS FUMES" WITH TRIMETHYLETHYLENE

Expt. No.			7^a	8^b	9^c	10^d	11^e	12^f	13^f	14^g	15^h	16^i
HNO$_3$ d^{20}			1.4138	1.4138	1.3054	1.3054	1.3054	1.3011	1.3011	1.30	1.312	1.312
Reaction	Time, mins.		90	60	120	120	120	150	300	60	120	120
	Temp., °C.		4	7	4	4	5	5	5	−12	3	3
Crude Product	Total, g.		26.0	36.0	27.0	19.0	33.0	16.0	20.7	26.0	10.0	17.4
	gave	(B) g. deposited	2.4		2.8		0.7	1.1		4.0	0.8	1.5
		during, hrs.	72		84		12	24		36	70	42
		(a) Blue Filtrate, g.	23.1		23.6		32.3	14.9		22.0	8.7	14.7
Distillation of Crude Product or Filtrate (a)	Oil used, g.		21.7	36.0	22.4	19.0	32.3	35.6		22.0	8.7	14.7
	gave	(b) Blue dist. Total g.	7.8	18.3	9.4	10.5	15.3	17.2		8.7	3.8	9.1
		deposited (B) g.		1.2		3.3		3.6			0.1	
		deposited during hrs.		40		60		36				
		(c) Residual Green Oil, g.	13.9	16.9	12.6	8.8	17.2	17.6		9.5	4.6	5.4
Sulphone from Oil (c)	Oil used, g.			2.0	3.0	2.0					3.8	4.3
	NaNO$_2$, g.				0.5	0.4					0.45	0.6
	gave	Crude thioether, g.		2.8	2.1	2.0					2.8	3.2
		Sulphone (N), g.		1.1	0.35	0.7					1.4	1.0
Fractionation of Blue Oil (b)	Oil (b) used, g.			16.1	9.1	6.7	15.3	12.8			3.0	8.7
	gave	(d) Blue dist. Total g.		9.7	7.0	2.8	12.4	9.2			2.0	6.4
		deposited (B) g.					2.7					
		deposited during hrs.					36					
		(e) Residual Green Oil, g.		5.2	1.7	3.4	2.7	3.3			1.0	2.0
% (B)			9.4	3.4	13.2	17.4	11.2	13.0		11.0	9.0	8.6

See notes on following page.

Notes to Table II

Experiment 15 was made with 15 g. of trimethylethylene and 45 cc. of ether; otherwise 20 g. of the alkene and 60 cc. of ether were used. Generally 120 g. of technical arsenous oxide and 80 cc. of nitric acid were used; in 12 and 13, 200 g. of the oxide reacted with 100 cc. of the acid and, in 16, 120 g. of the analytical grade of the oxide with 80 cc. of the acid. Letter B designates $[(CH_3)_2C(NO_2)CH(NO)CH_3]_2$; C the dinitro compound, $(CH_3)_2C(NO_2)CH(NO_2)CH_3$; M an alcoholic solution of sodium thiophenylate (prepared by dissolving two equivalents of sodium, assuming that the analysed oil consisted entirely of C, in 20–25 cc. of methyl alcohol and adding the corresponding amount of thiophenol); and N the sulfone, $(CH_3)_2C(SO_2C_2H_5)CH(NO_2)CH_3$.

[a] Filtrate *a*, at 2 ± 2°, deposited 0.05 g. of B during 43 days. In duplicate experiments, 5 g. of oil *c*, with M, gave: 0.9 g.; 1.0 g. of $NaNO_2$ and (*1*) 4.3 g.; (*2*) 4.6 g. of oily product. The combined oils distilled to give: (*1*) 1.1 g. (b.p. 43–45° at 2 mm.), and (*2*) 6.0 g. of oil, b.p. 132–135° at 2 mm.; oxidation of 1 g. of *2* gave 0.7 g. of N.

[b] Distillate *d*, b.p., 38–50° at 2 mm., decomposed when distilled at ordinary pressure.

[c] Filtrate *a*, at 2 ± 2°, deposited 0.75 g. of B during 50 hours. Oil *c*, mol. wt., 213. Oil *e*, with M, gave 0.5 g. of $NaNO_2$ and 1.6 g. of oil which was oxidized, yielding 1 g. of N.

[d] Distillate *b* deposited B: the filtrate gave distillate *d*, b.p. 30–34° (nearly all at 31–32°) at 2 mm., and the residual, bluish-green oil *e*. Oil *e* gave: 2 g. of blue distillate, b.p., 50–55° at 2 mm., and 0.6 g. of residual, green oil, which, with M, gave 1.5 g. of oil, yielding, after oxidation, 0.5 g. of N.

[e] Oil *c* steam-distilled: the residual oil (2.5 g.) was not investigated; the volatilized oil (10 g.) distilled, at 2 mm., to give 4 g. of blue distillate (not investigated) and 6 g. of residual, green oil which solidified at −80°. Adhering oil was separated from the bluish wax (4.5 g.; m.p. 40–50°) with an inverted filter; recrystallization at −80° gave 2.1 g. of pale blue wax, which was sublimed at low pressure and gave pure *C*. The oily material (3.3 g.) isolated during purification of *C* gave, with M, 1.2 g. of impure $NaNO_2$ and 3.5 g. of oily product which was oxidized, and yielded 1.9 g. of N.

[f] Filtrate *a* of 12 and the total product of 13 were combined. Oil *c*, mol. wt., 235; 15 g. of the oil, distilled with steam, gave: (*1*) 8 g. of blue distillate, and (*2*) 4.4 g. of residual green oil of mol. wt., 273. From oil (*2*), at 100° at low pressure, a small amount of material volatilized, leaving a residual oil of mol. wt. 360. Using a fractionating column, a portion (7.8 g.) of blue oil (*1*) was separated into (*3*) 2.8 g. of blue distillate and (*4*) 5 g. of green, residual oil. Oil (*4*), distilled in a small Claisen flask at 2 mm., gave 3–4 drops of easily volatile blue liquid and a colorless wax. With M, 4.6 g. of the wax gave 5 g. of an organic product (*f*); oxidation of 2 g. of *f* yielded 1.6 g. of N.

A portion (2.5 g.) of (*3*) was fractionated and gave (*5*) 1.2 g. of blue distillate (n_D^{20} 1.4433; *Anal.* Found: C, 48.75; H, 8.04) and (*6*) 1 g. of residual blue oil, n_D^{20} 1.4482, from which 0.05 g. of B separated during 24 hours.

Distillate *d*, with the bath-temperature at 32°, gave (*7*) 4.1 g. of bluish distillate (*Anal.* Found: C, 49.96; H, 7.37) and (*8*) 5.1 g. of bluish-green, residual oil, which, after extraction with 5% alkali, gave: C, 48.13; H, 7.18. A solution of 3.8 g. of (*7*) in 10 cc. of ether was saturated with dry HCl at 0°: after 15 hours, solvent and excess HCl were removed *in vacuo,* the residual oil was diluted with ether, and the solution was washed with water. Solvent was removed *in vacuo* from the dried solu-

Accordingly, the lower yields of compound III, obtained when it was isolated from the crude and from the distilled, blue oils separately, are not attributable to decomposition during distillation. In an atmosphere of nitrogen, although the technical and the analytical grades of arsenous oxide were used, respectively, in experiments 15 and 16, the reaction products yielded nearly the same proportion (9.0 per cent. and 8.6 per cent.) of compound III; an indication that the composition of the gaseous reactant was the same in the two experiments. But the agreement in the relative yields of the dimeric compound may have been accidental, for the yields of total product in these two experiments differed greatly and, in subsequent experiments, neither with moist "nitrous fumes" (experiments 20–22, Table IV), nor under anhydrous conditions (experiments 23–26, Table IV) were concordant results obtained. The yield (20 per cent.) of compound III obtained with dried gas generated from nitric acid of density 1.35 (experiment 23, Table IV) is higher than the best yield (17.4 per cent.) obtained with moist gas (experiment 10, Table II), but the difference, in view of the wide variation (20 per cent.) in the results obtained under anhydrous conditions, is not significant. With dry "nitrous fumes" at −80°, a product was formed which decomposed briskly below 0°, with evolution of gas, leaving an oil from which compound III separated in a yield of 20 per cent. (experiment 28, Table IV). In view of this result, the inconsistent yields of compound III, with respect to reaction temperature, may be attributable to a primary formation of a reaction product, which undergoes spontaneous decomposition to yield products isolable under ordinary conditions. Although our experimental conditions, much more than those of Schmidt, favored the formation of derivatives of nitrogen

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tion; the residual oil, with a solution prepared from 1.5 g. of Na, 30 cc. of methyl alcohol and 7.3 g. of thiophenol, gave 3.4 g. of oily product, and oxidation of 1.5 g. of the latter oil yielded 0.5 g. of N.

Oil *e*, treated with M, gave 0.9 g. of $NaNO_2$ and 2.6 g. of oil, yielding, after oxidation, 1 g. of N.

[g] Distillate *b* was fractionated and gave: (*1*) pale green oil, b.p., 32° at 4 mm.; n_D^{20} 1.4375; (*2*) blue oil, b.p., 44–46° at 2 mm.; n_D^{20} 1.4470 (*Anal.* Found: C, 46.49; H, 7.59; N, 14.87); and (*3*) blue residue, n_D^{20} 1.4480.

[h] Distillate *b* deposited 0.1 g. of B: a portion (3 g.) of the filtrate gave blue distillate *d*; n_D^{20} 1.4411 (*Anal.* Found: C, 48.00; H, 7.47), and oil *e* which, with M, gave 0.8 g. of oily product, yielding, after oxidation, 0.2 g. of N. A solution of 1.2 g. of *d* in 10 cc. of ether, saturated with HCl at 0°, was treated as described above, and the washed and dried product was analysed: 0.2315 g. gave 0.0410 g. AgCl. Oil *c*, mol. wt. 226.

[i] A portion (8.7 g.) of distillate *b* was fractionated, and gave distillate *d*; n_D^{20} 1.4416 (*Anal.* Found: C, 48.78; H, 7.55), and oil *e* which, with M, gave 1.8 g. of oily product, yielding, after oxidation, 0.7 g. of N. A solution of 1.9 g. of *d* in ether, saturated with HCl, was treated as above: the residual oil was analysed, 0.2789 g. gave 0.695 g. AgCl. Oil *c*, mol. wt., 253.

trioxide, the results were not reproducible, nor reconcilable with the experimental conditions, and under no conditions could the high yields (55–66 per cent.) of Schmidt's "bis-nitrosite" be approached.

The liquid products formed by the action of "nitrous fumes" upon trimethylethylene in ether solution were separated by low pressure distillation into an easily volatile, blue distillate (oil *b*, Table II), representing approximately 50 per cent. of the reaction product, and a much less volatile, green oil (oil *c*; Table II) from which, as the only pure product, a 6 per cent. yield of a waxy product was isolated in experiment 11 (Table II). This wax is identical with that formed from nitrogen tetroxide and trimethylethylene, and hitherto has been considered as the nitro-nitrite derivative of trimethylethane[1b], $(CH_3)_2C(ONO)CH(NO_2)CH_3$; mainly because of the facile and quantitative conversion, with sodium thiophenylate, to the corresponding thio-ether, $(CH_3)_2C(SC_6H_5)CH(NO_2)CH_3$. However, the wax is reduced catalytically to isoamylenediamine, and, consequently, must be the dinitro addition product of 2-methylbutene-2, $(CH_3)_2C(NO_2)CH(NO_2)CH_3$(IV). Although a part of the dinitro compound (IV) was volatilized during low-pressure distillation and could be recovered as a greenish oil (oil *e*, Table II) by fractionation of the distilled blue oil (oil *b*, Table II), a semi-quantitative separation of the dinitro compound was not possible; the best separation was effected by steam-distillation, but the method is unsatisfactory because some of the product is decomposed, and the volatilized oil contained, besides 70–80 per cent. of the dinitro compound, unidentified blue, or greenish-blue, products. Indirect determinations, made by treating portions of the crude green oil (oil *c*, Table II) with alcoholic sodium thiophenylate and oxidizing the thio-ether thus formed to the corresponding sulfone[1b], showed that the dinitro compound (IV) constituted 14, 16, 8.5, 12 and 7 per cent., respectively, of the products in experiments 7, 8, 12, 13, 15, and 16. Although the pure sulfone is fairly resistent to the action of chromic anydride, as oxidant for the crude thio-ether, the anydride proved unsatisfactory because in several experiments the oxidation was destructive. With hydrogen peroxide, beside the sulfone, oily products were sometimes produced, which resisted the action of the peroxide, but were destructively oxidized by chromic anhydride. Neither with the anhydride, nor with the peroxide, was the yield of sulfone equivalent to the yield of sodium nitrite formed in the reaction with sodium thiophenylate and, although the salt may have been formed, in part, from other products than the dinitro compound (IV), the yields of the sulfone are considered only as minimum values. Experiments showed that the nitroso-nitro compound (III), by treatment with "nitrous fumes" in benzene, or with ozone in chloroform, is oxidized to the dinitro compound (IV). However, while the appearance of the dinitro compound in the addition products, formed from "nitrous fumes", may be attributed, in part, to oxidation of compound III, or the corresponding, primarily-formed, monomeric nitroso-nitro derivative, yet, because nitrogen dioxide adds very facilely to the alkene, the dinitro compound probably is mainly formed by direct addition of the dioxide. Accordingly, the yield of the dinitro compound (IV) should depend upon the composition of the "nitrous fumes", but a definite correlation is not established by the results of our experiments.

Molecular-weight determinations indicated that the green oil (oil *c*, Table II), which did not distill at the pressure of a mercury pump, contained products of high molecular weight; the values 213, 235, 226 and 253 were obtained, respectively, in experiments 9, 12, 13, 15, and 16. These values varied with the extent of separation of the volatile products attained by low-pressure distillation. After removing, by steam-distillation, the major part of the dinitro compound (IV) from the crude oil, in experiments 12 and 13, the residual green oil gave the value 273 in a molecular-weight determination, but, after heating to 100° at the pressure of a mercury pump, a small amount of oil, apparently impure dinitro compound (IV), volatilized, leaving a very viscous oil of molecular weight 360. The chemical nature of the viscous liquids, constituting 10–20 per cent. of the reaction product, could not be determined: probably the products are formed by the action of "nitrous fumes" upon polymers of trimethylethylene, which are rapidly formed by the action of strong acids upon the alkene.

The distilled blue reaction product (oil *b*, Table II) in experiments 8, 10, 12, 13, and 15, deposited the recorded amounts of the dimeric nitroso-nitro compound (III). The filtrates in these experiments, and the distilled blue oils (oil *b*, Table II), from which no dimeric product separated in experiments 9, 11, and 16, were fractionated (at 2 mm.) with an efficient column, and gave blue distillates (oil *d*, Table II) and greenish residual oils (oil *e*, Table II) of which the dinitro compound (IV) constituted 20–50 per cent., as determined indirectly by converting the dinitro compound to the corresponding phenylsulfone. The intensely blue distillate (oil *d*, Table II) was a mixture of products and, in experiment 11, deposited a 22 per cent. yield of the dimeric compound III; usually no solid appeared after the second distillation. By redistilling the blue oil very slowly, a markedly less colored fraction (fraction I, Table III) was obtained, which gave values on analysis closely approaching those calculated for 2-methyl-3-nitrobutene-2 ("nitroamylene")[8].

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[8] Haitinger [*Monatsh.*, **2**, 290 (1881)], by the action of concentrated nitric acid upon tertiary amyl alcohol, obtained mainly oxidation products and a low yield of impure "nitroamylene." The synthesis undoubtedly proceeded through the preliminary formation of nitrous fumes and isopentylene-2.

These results led us to the conclusion that the fractionated blue oils consisted mainly of the depolymerized nitroso-nitro compound (III) and nitroamylene. No direct relationship is discernable between the refractive indices and the analytical data, but the irregularities may be attributable to variations in the refractivity of dissolved nitroso-nitro compound (III), whose refractivity varies with the degree of polymerization, concentration, and solvent[6]. An attempt to estimate the concentration of the nitroamyl-

TABLE III

FRACTIONATION OF PRODUCTS

EXPT. NO.	FRACTIONS	GRAMS	n_D^{20}	% C	% H	NITROALKENE, %
7[a]	I	1.3	1.4364			
	II	2.6	1.4405			
	III	2.7	1.4485			
9[b]	I	2.9	1.4426	51.94	7.88	99
	II	1.3	1.4447	50.10	7.56	80
	III	2.6				
	IV	1.9	1.4480	47.22	8.74	50
10[c]	I	0.95	1.4365	51.17	7.61	96
	II	0.95	1.4382	50.82	7.93	90
	III	0.90	1.4416			
11[d]	I	1.7	1.4381	51.53	7.88	95
	II	2.8	1.4408			
	III	3.8	1.4449			
	IV	3.5	1.4440	48.70	7.22	69

Distillate *d* (Table II) in experiments 9, 10, and 11 and distillate *b* (Table II) of experiment 7 were redistilled very slowly and gave fractions I–III of Table III: the bath temperature was 30–35°; 40° in experiment 7. An all-glass condensing apparatus, cooled to −25°, was used; distillation temperatures could not be determined. The nitroalkene content was estimated from the analytical data, assuming that the distillates contained only the nitroalkene and compound III.

[a] Distillate *b* (Table II) gave fractions I–III.

[b] Distillate *d* (Table II) gave fractions I–III; residual oil III was distilled in a small Claisen flask and gave 1.9 g. of blue distillate (IV), b.p., 95–102° at 60 mm., leaving 0.5 g. of green residual oil.

[c] Distillate *d* (Table II) gave fractions I–III. The distillates, at 2 ± 2°, deposited no solid during 14 days, and were then analysed: the refractive index of fraction I had changed to 1.4373 at 20°; the value for fraction II remained at 1.4383 at 20°.

[d] Distillate *d* (Table II) (b.p., 35–42° at 2 mm.; bath temperature 70°) deposited 2.7 g. of the dimeric compound III; the filtrate (9.1 g.) yielded 0.3 g. of the same solid. The filtrate (8.3 g.) gave fractions I–III; residue III was distilled and gave distillate IV.

ene, by comparing the refractive indices of the blue distillates with those of the supposed components, failed; the difference between the values of the respective compounds is apparently small, and the monomeric nitroso-nitro compound (III), prepared by depolymerization of the bis-derivative at 70–80°, completely repolymerized to the crystalline solid within 2–3 minutes, with a rapid shift in the refractive index. Estimation of the composition of the liquid, assuming the oil to contain only the above-mentioned two components, was made on the basis of analytical data. The results indicated that the fractionated blue oils contained 70–80 per cent. of the nitroalkene; accordingly, the latter constitutes 10–20 per cent. of the reaction product. A summary of typical fractionations, with related analytical data, is given in Table III. An indirect determination of the concentration of the nitroalkene was made by saturating the fractionated blue oil with gaseous hydrogen chloride and determining the amount of organic chloride formed. The results indicated the presence of 10–18 per cent of the nitroalkene in experiments 15 and 16. In experiments 12 and 13, the fractionated blue oil was saturated with gaseous hydrogen chloride, and the product, treated with alcoholic sodium thiophenylate, gave a crude thio-ether from which 2-methyl-3-nitro-2-phenylsulfonebutane was obtained in a yield of 15 per cent. Although this small yield does not agree with the analytical data, which indicates the presence of 70–80 per cent. of the nitroalkene in the blue oil, the low yield of the sulfone (experiments 12 and 13), and of the corresponding chloride (experiments 15 and 16), may be attributed to elimination of hydrogen chloride from the primarily-formed, tertiary chloride, which loses hydrogen chloride very easily. The formation of the sulfone, however, even in the above amount, showed definitely that 2-methyl-3-nitrobutene-2 constituted a not inconsiderable proportion of the reaction product, formed by the action of "nitrous fumes" upon trimethylethylene.

While catalytic reduction of the crude and of the fractionated, blue oils in alcohol solution, in the presence or absence of hydrogen chloride, soon stopped, in acetic acid the reduction, at first, proceeded rapidly, but the rate then decreased, and reduction was complete only after several days. Ammonia, in varying amounts, was formed in all reductions of the blue liquid products. Reduction of the fractionated oils (experiments 39–41; Table VI) yielded, together with other basic products, 2-methyl-3-aminobutane, which confirms the presence of nitroisoamylene-2 in the crude addition products. The yield of the easily volatile amine, identified through the *p*-nitrobenzoate, indicated that the crude blue oils (oil A) in experiments 39–41 contained, respectively, 7.8, 2.5 and 1.3 per cent. of the nitroalkene. These results, since the amine was difficult to isolate, are not so inconsistent as it would seem, and support the estimated concentrations of the nitroalkene based on the analytical data (Table III). The widely divergent estimates, though the values are considered as only very approximate, undoubtedly indicate that the concentration of the nitroalkene in the crude addition products varies with the conditions under which the latter product is formed. However, the accuracy of the method of estimation is not known, and a direct correlation of the yield with the experimental condition is, therefore, not possible.

Diamines have been obtained, generally in low yields, by reduction of the crude, and of the purified, solid products formed by the action of "nitrous fumes" upon ethylene[9a], propylene[9b], butene-1[9c] and isobutylene[9d], but Schmidt[6, 10], although a number of reduction methods were used, obtained basic compounds, other than ammonia, neither from the products prepared from trimethylethylene and "nitrous fumes", nor from those obtained with nitrogen tetroxide. Whereas the structure of the dimeric nitroso-nitrate (I) was definitely established by its chemical reactions[11], no direct evidence for the structure of the dimeric nitrogen trioxide addition product could be obtained, yet, because only ammonia was obtained upon reduction and treatment with organic bases apparently eliminated nitrogen dioxide, Schmidt[6] assumed that both nitrogen atoms could not be attached to carbon in the trioxide addition product and that it must have the nitroso-nitrite structure (II). However, since the trioxide derivative is catalytically reduced to isoamylenediamine, the nitroso-nitrite structure must be replaced by the nitroso-nitro formula (III)[12]. In the first reduction (experiment 31, Table V), the solvent was distilled *in vacuo*, and the residual syrup was alkalinized. Under these conditions, together with the diamine, some ammonia was liberated. Yet, hydrogen chloride, when bubbled into the acetic acid solution of the reduction product of experiment 32, precipitated only pure isoamylenediamine dihydrochloride (yield 87.8 per cent.) and, accordingly, catalytic reduction

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[9] (*a*) Demjanow, *Chem. Zentr.* **1899**, I, 1064; (*b*) *ibid.*, **1901**, II, 333; (*c*) *Ber.*, **40**, 245 (1907); (*d*) Ssidorenko, *Chem. Zentr.*, **1907**, I, 399.

[10] Schmidt, *Ber.*, **35**, 2336 (1902).

[11] The nitrate, with organic bases, yielded nitrolamines [Wallach, *Ann.*, **241**, 296 (1887)]; with KNC, "cyanoisopropylmethylketoxime," $CH_3C(NOH)C(CH_3)_2CN$ [Wallach, *Ann.*, **248**, 169 (1888)]; and, with sodium methylate, methylmethoxylisopropylketoxime [Schmidt and Austin, *Ber.*, **35**, 3722 (1902)]. It is not known whether these reactions proceed by direct or by pseudo-substitution, *i.e.*, by elimination and addition.

[12] The formation of nitroso-nitro addition products from mono- and diarylethenes has been demonstrated experimentally [*Ann.*, **328**, 154 (1903)] and, in view of these and Demjanow's results, Wieland [*Ann.*, **424**, 74 (1921)] suggested that nitrogen trioxide forms nitroso-nitro derivatives, so-called pseudonitrosites, with all alkenes and that Schmidt's "bis-trimethylethylene nitrosite" very probably belongs to this same group. No experimental evidence was given in support of this view.

does not eliminate much nitrogen, as ammonia, from the addition product. The diamine, as well as its dihydrochloride, yielded a crystalline dibenzoate, which proved to be identical with the dibenzoate prepared from the diamine formed by reducing the mono-, or the dihydrochloride of 2-methyl-2-aminobutanone-3 oxime[13] (experiments 35–37, Table V).

Formation of the nitro-nitrite of isopentane, $(CH_3)_2C(ONO)CH(NO_2)$-CH_3, by addition of nitrogen tetroxide to the alkene, the addendum functioning as $-ONO + -NO_2$, is theoretically possible and, indeed, the waxy addition compound, because its behavior towards sodium thiophenylate appeared to be analogous to that of the nitroso-nitrate (I), was assumed to be the nitrous ester. However, on reduction the products corresponding to the nitro-nitrite structure, ammonia and 2-methyl-3-aminobutanol-2, were not obtained, instead the waxy compound, whether prepared by the action of "nitrous fumes" or nitrogen tetroxide upon trimethylethylene, yielded isoamylenediamine (experiments 33 and 34, Table V) and, consequently, the waxy addition product must be the 2,3-dinitro derivative of isopentane. The diamine was identified through the toluenedisulfonamide and the dibenzoate. These products were identical with the corresponding derivatives of the reduction product of the bis-nitroso-nitro compound (III) and, also, of 2-methyl-2-aminobutanone-3 oxime.

Addition of nitrogen trioxide, with $-ONO$ and $-NO$ as the functional groups, may yield the nitroso-nitrite (II) which, in view of the facile conversion of the nitroso-nitro derivative (III) to the dinitro compound, may be oxidized, more or less completely, to the nitro-nitrite. But the latter product may also be formed by direct addition of nitrogen tetroxide to the alkene, and, like the nitroso-nitrite, would yield ammonia and 2-methyl-3-aminobutanol-2 on catalytic reduction. Consequently, through the reduction products, since a quantitative isolation was not realized, the presence of a mixture of the nitroso- and the nitro-nitrite in the blue oils could not be ascertained, nor did the volume of absorbed hydrogen give an insight into the composition of the product reduced. The nitrogen trioxide and tetroxide derivatives require, respectively, 5 and 6 moles of hydrogen for complete reduction, yet, since neither the original nor the reduced products could be separated semi-quantitatively, the relation between the volume of absorbed hydrogen and the composition of the liquid product, formed by the action of "nitrous fumes" upon trimethylethylene, is not apparent.

On reduction, the crude and the distilled blue products yielded ammonia,

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[13] In the preparation of this oxime, and in its reduction, we followed methods employed by Drew and Head [*J. Chem. Soc.*, **1934**, 49] for the preparation of isobutylenediamine.

but, although 2-methyl-3-aminobutanol-2, was probably formed in equivalent amount, but the amino alcohol could not be isolated, nor could crystalline derivatives be separated from the viscous oils obtained on acylation of the crude, or the distilled, reduction products (experiments 38–41; Table VI). While the yield of ammonia (experiment 41) indicated that the fractionated blue oil (oil A; Table VI) contained 21.5 per cent. of the nitro-nitrite derivative (II), the corresponding amino alcohol could not be isolated from the reduction products. The easily volatile 2-methyl-3-aminobutane was readily identified through the *p*-nitrobenzoate, but benzoylation of the higher-boiling amines yielded a viscous oil from which a very small amount of the dibenzoate of isoamylenediamine was isolated as the only crystalline and identifiable product. Acylation with *p*-nitrobenzoyl chloride gave, similarly, viscous, oily products, and camphorsulfonic acid, although it forms a crystalline salt with the isoamylenediamine (experiment 38), yielded an inappreciable amount of solid product with the high-boiling amines of experiment 39, and was not satisfactory as a means of separation of the basic reduction products. The diamine, undoubtedly derived mainly from the dinitro compound (IV), but possibly formed in part from the nitroso-nitro derivative (III), was isolated from the mixed amines as the dihydrochloride, but, as subsequent experiment showed, the salt, although only very slightly soluble in hot, secondary butyl alcohol, did not separate quantitatively from solutions containing an appreciable amount of the hydrochloride of 2-methyl-3-aminobutanol-2. Accordingly, the total yield of the diamine could not be determined, but, based on the yield of the isolated dihydrochloride (experiment 41), the diamine constituted at least 25 per cent. of the high-boiling reduction product. Almost the same yield (24 per cent.) of the diamine was isolated as the dibenzoate in experiment 38, but the concordance in the yields is probably accidental, and the values do not represent the total yield of the diamine.

The benzoylated reduction product (experiment 41, Table VI) yielded, on low pressure distillation, a viscous distillate and a residual oil, from which a small amount of the dibenzoate of isoamylenediamine was isolated. The distilled, viscous oil could not be crystallized, yet the crude product gave values on analysis in approximate agreement with those calculated for the benzoate of 2-methyl-3-aminobutane. While the separation of this easily volatile amine from the higher-boiling, basic products may have been incomplete in experiment 41, the separation was undoubtedly complete in experiment 38. Yet oily benzoylation products were obtained with the mixed amines, and in yields increasing with the boiling-point of the base acylated. Accordingly, since the reduction product (experiment 38, Table VI) boiled at a slightly higher temperature than isoamylenediamine and, since benzoylation of the pure diamine yielded a product which crystallized readily (experiments 31–37, Table V), the oily benzoates of experiments 38–41 (Table VI), largely because of the appearance of ammonia in the crude reduction products, appeared to be derived in part from 2-methyl-3-aminobutanol-2 which, as subsequent experiments showed, yields oily acylation products that are difficult to crystallize and purify. The bis-nitroso-nitrate (I) was reduced catalytically (experiments 29 and 30, Table V) and, in accord with the previously determined structure[11], yielded, together with ammonia, 2-methyl-3-aminobutanol-2, but the easily soluble benzoate, and the toluene sulfonamide of the amino alcohol, crystalline products identical with the corresponding derivatives of the amino alcohol prepared from amylene bromohydrine, were obtained in varying and generally low yields, notwithstanding the fact that the amino alcohol used in the acylation was essentially pure. Accordingly, failure to isolate derivatives of the amino alcohol from the viscous oils obtained on acylation of the reduction products of the crude and the distilled blue oils (experiments 38–41, Table VI) may be attributed to the difficulty of isolating and crystallizing the relatively soluble acylation derivatives of the amino alcohol. Although the isolation was not realized, the amino alcohol was probably formed, yet our results do not definitely establish that nitrogen trioxide yield an addition product in which nitrogen is attached to carbon through oxygen.

EXPERIMENTAL

General procedure.—The trimethylethylene was prepared by heating tertiary amyl alcohol with 10% hydrochloric acid[14] and after fractionation, had the following properties: b.p., 37.5–38.5°; n_D^{20} 1.3872.

The three-necked reaction flask, provided with a mechanical stirrer and a thermometer, was connected by a glass tube, the lower end of which dipped below the ethene solution, to the top of a reflux condenser, which was attached to a 1-l. flask, charged with nitric acid and arsenous oxide, mixed with glass wool to prevent caking. The technical grade of arsenous oxide was used, except in experiments 16 and 22 in which the analytical grade was employed. In experiments 4–6, 15–16, 17–22, and 24–28, a 500-cc. flask, provided with a ground-glass joint and sealed-in tubes required to flush the apparatus with nitrogen, was sealed to the lower end of a reflux condenser. The latter was attached at the upper end, by a bent tube, to a 100-cc. bulb, which terminated in a tube extending below the ethene solution, contained in a three-necked flask provided with a stirrer, thermometer, and an exit tube of the bubble-counter type. The gas evolution was slow at ordinary temperature, and the generator was therefore heated in a boiling water bath, except in experiment 16 when the temperature was 45–50°. The reaction mixture was diluted with ether, except in experiment 27 (see notes, Table IV); suspended solid, if present, was removed by filtration, and the ether solution was washed with cold water, except in experiment 25 (see notes, Table IV). Solvent was removed from the dried ether solution *in*

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[14] MICHAEL AND ZEIDLER, *Ann.*, **385**, 259 (1911).

vacuo, and the blue residual oil was distilled immediately, or after the dimeric compound III had separated. An all-glass apparatus, attached by a heavy rubber tube to a mercury vapor pump was used in the low-pressure distillations. The blue distillate (oil *b*, Table II) was refractionated at 2 mm., using a small modified Podbielniak column, and gave distillate *d* and residual oil *e*. In experiments 7, 14, and 23, the distillates were treated as described in the notes to Tables II, III and IV. In the distillations, the bath-temperature was gradually raised (during 2–3 hours) to 80°; the distillation temperatures were not recorded, except when the bath-temperature was kept constant (experiments 10 and 11). This distillation effected a separation of the more volatile products from the dinitro derivative (IV). Fraction *d* (Table II) was redistilled and gave fractions I–III (Table III).

A portion of the non-volatile green residual oil (*c*, Table II) was added to an alcoholic solution of sodium thiophenylate, most of the solvent was distilled and the inorganic salt was filtered off, if present in appreciable quantity. Solvent was distilled *in vacuo* from the filtrate, or from the partially concentrated reaction mixture, when no inorganic salt was isolated. The residual mixture was shaken with water and ether, the ether solution was washed with dilute alkali and dried, and the solvent was removed. The residual oil, or a portion, was oxidized with chromic anhydride, or with 30% hydrogen peroxide. The chromic anhydride, in weight equal to the crude thio-ether, was added in small portions to the hot, acetic acid solution of the thio-ether, the mixture was heated 5–10 minutes on a steam-bath and poured into ice-water (experiments 8, 10, and 11); the pure sulfone generally separated; if not, the oily products were re-oxidized. In the oxidations with hydrogen peroxide, the oils, dissolved in 5–10 cc. of glacial acetic acid, were treated with 4–5 times the required amount of 30% hydrogen peroxide, and sufficient acetic anhydride was added to give a clear solution. The temperature was not allowed to exceed 40°; after the vigorous reaction was completed, the solutions were kept at room-temperature for 12–15 hours and were then added to ice-water. The precipitated sulfone was generally pure; if not, it was purified by sublimation at low pressure.

Preparation of products used for reduction.—The experimental procedure previously described was followed and all the preparations were made in an atmosphere of nitrogen. The liquid product of experiment 23, which was made in air, and the oily products of experiments 27 and 28 were not reduced. Technical arsenous oxide (120 g.), 80 cc. of nitric acid, 20 g. of trimethylethylene, and 60 cc. of ether were used, except when the analytical grade of the oxide (experiment 22) and 60 cc. of petrol (experiment 27) were used. In experiments 17–22 and 27 moist, in experiments 23–26 and 28, dry "nitrous fumes" were used; in experiments 23 and 24 the gas passed, successively, through calcium chloride and phosphoric anhydride, but through two tubes of the anhydride in the other experiments. The results are summarized in Table IV. Letter A designates $[(CH_3)_2C(ONO_2)CH(NO)CH_3]_2$, and B the nitroso-nitro compound, $[(CH_3)_2C(NO_2)CH(NO)CH_3]_2$.

Catalytic reduction.—Acetic anhydride (50 cc.) was used as solvent in experiment 29, and glacial acetic acid (50 cc., except that 25 cc. was used in experiment 33) in the other experiments. At first, reduction of the solid addition products, the crude and the fractionated blue oils, proceeded rapidly in glacial acetic acid with platinum oxide catalyst, but the rate of reaction then dropped off suddenly and addition of fresh catalyst increased it for a short period only. Catalyst was removed by filtration, hydrogen chloride was bubbled into the filtrate, and the solid product (ammonium chloride, or, in experiment 32, the dihydrochloride of isoamylenediamine) was removed by filtration. Solvent was distilled at reduced pressure

TABLE IV

PREPARATION OF PRODUCTS FOR REDUCTION

EXPT. NO.		17	18	19	20	21[a]	22	23[b]	24[c]	25[c]	26[d]	27[e]	28[f]
HNO$_3$, $d^{20°}$		1.311	1.311	1.311	1.242	1.242	1.247	1.35	1.3075	1.3075	1.3075	1.242	1.3075
Reaction	Time, mins.	150	210	120	180	420	300	120	120	120	120	180	120
	Temp., °C.	3–5	0–3	0–7	−20	0–3	−10	−20	−20	−20	−15	−20	−80
Product	Total g.	24.5	17.3	20.6	13.7	20.3	22.8	10.5	23.9	23.7	26.1	12.1	11.5
	(B), g.	0			1.75	1.0		2.1	3.9	1.2	2.6	0.2	2.3
	(A), g.	0										2.3	
% (B)		0		0	12.8	4.9	0	20	16.3	5.06	10	1.6	20

[a] After 3 hours, a test indicated that 14.2 g. of product had formed; 80 cc. of nitric acid (density 1.242) was added to the partially spent acid-oxide mixture, and gas absorption was continued for 3 hours.

[b] On steam-distillation the blue oil (7.5 g.) gave 4.5 g. of blue, and 0.7 g. of green, distillate, leaving 0.7 g. of green residual oil; the distillates deposited no solid.

[c] The filtrates deposited no solid during 11 days at 2 ± 2°; the reaction product in experiment 25 was not washed with water.

[d] The reaction product deposited 1.7 g. of B, and the filtrate yielded 0.9 g. of B.

[e] Solid (A, 1.6 g.) was removed by filtration; the heavy blue oil (*1*) was separated from the petrol solution (*2*). An ether solution of *1* was washed with water, dried and the solvent distilled *in vacuo*: the residual oil (4.6 g.) deposited 0.6 g. of A; the filtrate deposited 0.2 g. of B. Petrol solution *2* was washed with water and dried, and the solvent was distilled *in vacuo*; the residual oil (6 g.) deposited 0.2 g. of A.

[f] The "nitrous fumes" deposited solid nitrogen tetroxide in the cold gas-entrance tube. The reaction product evolved gas below 0° and about $\frac{1}{3}$ of the solution was suddenly blown out of the flask: the residual solution (60 cc.) was washed with water and dried, and the solvent was distilled *in vacuo*. The residual oil (11.5 g.) deposited 1.5 g. of B during 10 hours; the filtrate deposited 0.8 g. of B during 9 days at 2 ± 2°.

from the filtrate, the residue was diluted with secondary butyl, or tertiary amyl, alcohol and the solid product (ammonium chloride, or, in experiments 32 and 33, the dihydrochloride of isoamylenediamine) was removed by filtration. Solvent was distilled *in vacuo* from the filtrate, and left syrupy products which, in some experiments, could not be identified; in other experiments, the regenerated, basic products were distilled and converted to crystalline derivatives, which were identified. Conversion to the benzoyl and the *p*-toluenesulfone derivative was made in the usual way; the reaction mixture was heated on a steam bath for about one-half hour. Solid products were filtered off, washed with water, dried and recrystallized from a benzene-ether solution. When an oily product was formed, the mixture was extracted with chloroform, the solution was washed, dried; the solvent was distilled *in vacuo*, and the residue was crystallized from a benzene-ether solution. Identity of the crystalline derivatives of 2-methyl-3-aminobutanol-2, and of isoamylenediamine, was established by comparison with the respective derivatives of the amino alcohol and of the diamine, prepared as described below. In the reduction experiments (29–34), the solid addition products yielded the results given in Table V.

Preparation of 2-methyl-3-aminobutanol-2 and derivatives.—Isoamylene bromohydrine (43.2 g.) was added to aqueous ammonia (200 cc., saturated with the gas at 25°), and the mixture was shaken for 36 hours (petrol extracted 4.8 g. of colorless oil). The basic aqueous solution was distilled at ordinary pressure until the temperature of the vapor reached 102°. The cooled residual liquid was saturated with potassium hydroxide, extracted with ether, and the dried extract, on fractionation, yielded: (*1*) 1.4 g., b.p. up to 161.5° (mainly ether); (*2*) 11.9 g. of the aminoalcohol, b.p., 161.5–165°; and (*3*) 0.5 g. of residual oil.

(*a*) *Toluenesulfonamide.*—One gram of (*2*), treated with 3.7 g. of *p*-toluenesulfonyl chloride in the usual manner, yielded 2.2 g. of oily product which gave 1 g. of the sulfonamide (m.p. 127–129°: *Anal.* calc'd for $C_{12}H_{19}NO_3S$; C, 56.1; H, 7.4; N, 5.41; S, 12.45. Found C, 56.22; H, 7.48; N, 5.64; S, 12.44).

(*b*) *Benzoate.*—Benzoylation of 1 g. of *2* gave 2 g. of oily product, from which 1 g. of crystalline benzoate, m.p. 95–96°, was isolated. (*Anal.* calc'd for $C_{12}H_{17}NO_2$; C, 69.5; H, 8.2; N, 6.86. Found C, 69.66; H, 8.47; N, 6.85). The remainder of the product could not be separated from adhering oil.

Reduction of crude and fractionated blue oils.—The reductions were made in the usual manner with platinum oxide catalyst. When reduction stopped (experiments 38–40), catalyst was removed by filtration, solvent was distilled *in vacuo*, the residual syrup was alkalinized, and the mixture was extracted with ether. The dried ether solution gave the indicated fractions. In experiment 41, gaseous hydrogen chloride was bubbled into the filtered acetic acid solution of the reduction products, the precipitated ammonium chloride was removed by filtration, solvent was distilled *in vacuo*, and the residual syrup, treated as before, gave fractions *a*–*3*. The residual green oil (oil G; experiment 39) could not be reduced catalytically. The amines were acylated in the usual manner: acylation with *p*-nitrobenzoyl chloride was made in the cold, but, with benzoyl, or toluenesulfonyl, chloride, the reaction mixtures were heated on the steam bath for about one-half hour. Letter O designates the dibenzoate of isoamylenediamine, P the hydrochloride, and Q the *p*-nitrobenzoate of 2-methyl-3-aminobutane. The results are tabulated in Table VI.

Oxidation of nitroso-nitro compound (III): (*a*) *With "nitrous fumes".*—The moist gas generated from 60 g. of technical arsenous oxide and 40 cc. of nitric acid (density 1.416 at 20°) was passed, during ½ hour, into a mechanically stirred solution of 3 g. of the bis-nitroso-nitro compound in 25 cc. of benzene. The brown solution was

TABLE V

REDUCTION OF SOLID ADDITION PRODUCTS

Expt. No.			29^a	30^b	31^c	32^d	33^e	34^f	35^g	36^h	37^i
Product Reduced, g.	Isopentane deriv.	Bis-Nitroso-nitrate	8.7	10							
		Bis-Nitroso-nitro-			10	9.5					
		Dinitro-					5.5	4.9			
	2-Methyl-2-amino-butanone-3 oxime salt	HCl							7		
		2HCl								7	5.7
Hydrogen absorbed		Liters	5.11	5.33	7.55	7.39	4.01	3.94			
		Time, hrs	27.6	22		12.6	32	20			
Product (P)		Hydroxy-amine, g	1.8	2.0							
		B.p., °C	140–160	160–200							
		Diamine, g			1.1						
		B.p., °C			139–143						
		Diamine 2HCl, g				10	3.1	3.7	0.7	0.8	1.4
Acylation	Gave benzoate of	Sample P, g	0.8	0.8		0.5	1.0	1.0	0.7	0.8	1.4
		Hydroxy-amine, g	0.7	0.2							
		M.p., °C	95–96	95–96							
		Diamine, g				1.0	1.4	1.8	0.9	0.8	0.75
		M.p., °C				147–148	147–148	147–148	147–148	147–148	147–148
	Gave tosyl deriv. of	Sample P, g	1.0	1.0	0.9	0.5					
		Hydroxy-amine, g	1.9	1.0							
		M.p., °C	128–129	128–129							
		Diamine, g			1.0	0.8					
		M.p., °C			162–163	162–163					

See notes on following page.

Notes to Table V

[a] The bis-nitrate was reduced in acetic anhydride, catalyst was filtered off, solvent was distilled *in vacuo*, the residual syrup was heated with dilute hydrochloric acid for 4 hours and the solution evaporated to dryness *in vacuo*. The residue, when warmed with secondary butyl alcohol, yielded 1.3 g. of ammonium chloride. Solvent was distilled *in vacuo* from the filtrate and the syrupy residue, when alkalinized at 0°, yielded an oil which gave fractions: (*a*) 0.3 g., b.p. up to 140°; (*b*) 1.8 g., b.p. 140–160° (mostly at 150–155°); and (*c*) 0.2 g. of residual oil.

[b] The filtered solution of the reduction product yielded, with gaseous HCl, 1.3 g. of ammonium chloride. The syrupy hydrochloride was alkalinized at 0°, and the liberated oil was fractionated, yielding: (*a*) 0.4 g., b.p. up to 160°, and P, 2 g., b.p. 160–200°. A mixture of the toluenesulfonamide with that of experiment 29 melted at 127–129°.

[c] The filtered solution of the reduction product was concentrated *in vacuo*, and the resulting syrup was made alkaline at 0°. The dried ether solution was fractionated, yielding, besides the ether distillate: (*a*) 0.05 g., b.p. 56°; P, 1.1 g., b.p. 139–143°, and (*b*) 0.3 g. of residual oil. The basic, aqueous solution was distilled, and the distillate (20 cc.; $\frac{1}{3}$ of the original solution), was acidified with gaseous HCl and evaporated to dryness, yielded 5.2 g. of ammonium chloride.

[d] Hydrogen chloride precipitated 5.3 g. of solid (*1*) from the acetic acid solution of the reduction product. The filtrate, evaporated *in vacuo*, yielded a paste from which secondary butyl alcohol precipitated 4.7 g. of solid (*2*), m.p. 290° with decomposition; the alcohol solution yielded 2.2 g. of syrup, which could not be identified. The combined solids (*1* and *2*; 9.6 g.) were alkalinized, and the mixture was heated to 100°, but evolved no ammonia. The cooled mixture was extracted with ether, and the dried extract was fractionated, yielding: (*a*) an ether distillate, which, with gaseous HCl, yielded 4.6 g. of the dihydrochloride of isoamylenediamine (*S*: *Anal.* calc'd for $C_5H_{16}Cl_2N_2$; Cl, 40.6. Found: Cl, 40.6); (*b*) 0.3 g., b.p. up to 135° (mostly ether); and (*c*) 2 g. of basic liquid, b.p., 135–138°, from which a benzoate and a toluenesulphonamide was prepared. (*Anal.* of benzoate: calc'd for $C_{19}H_{22}N_2O_2$: C, 73.50; H, 7.15; N, 9.03. Found; C, 73.52; H, 7.03; N, 8.96. *Anal.* of sulfonamide; calc'd for $C_{19}H_{26}N_2O_4S_2$; C, 55.56; H, 6.39; N, 6.83; S, 15.57. Found: C, 55.57; H, 6.11; N, 6.82; S, 15.34.)

One gram of solid yielded 1.2 g. of the dibenzoate of isoamylenediamine, m.p. 147–148°, identical with the dibenzoate prepared from c.

[e] Nitrogen tetroxide (22.6 g.) was added, during 2 hours, to a mechanically-stirred solution of 25 g. of trimethylethylene in 75 cc. of ether, cooled to −6°. The blue, oily product (43.6 g.) was steam-distilled, and the volatilized oil was fractionated, yielding: (*1*) 17.5 g. of blue distillate, and (*2*) 6.8 g. of pale-green wax, which, crystallized from ether at −80°, gave the dinitro compound (5.5 g.; m.p. 30–40°) used in the reduction experiment. When boiled with secondary butyl alcohol, the syrupy hydrochloride of the reduction product yielded 3.1 g. of the dihydrochloride of isoamylenediamine (*Anal.* calc'd for $C_5H_{16}Cl_2N_2$; Cl, 40.6. Found: Cl, 40.5) and 2.7 g. of syrup; the syrup was made alkaline, the mixture was extracted with ether and the dried extract gave, with gaseous HCl, a gummy hydrochloride, which could not be identified.

[f] In two experiments, moist "nitrous fumes", generated from 80 cc. of nitric acid (density 1.315 at 20°) and 120 g. of technical arsenous oxide, were bubbled, during 2–4 hours, into ether solutions of trimethylethylene (20 g.), cooled to −7°. The preparations were made in an atmosphere of nitrogen. The crude products (33.2

Notes to Table V—Continued

g. and 32 g., respectively) were combined and distilled at the pressure of a mercury pump, yielding: (*1*) 28.1 g. of blue distillate, and (*2*) 33.1 g. of green residual oil, which was steam-distilled. The volatilized oil, distilled at 2 mm., gave: (*a*) 7.8 g. of blue distillate, and (*b*) 12.7 g. of green residual oil, which was distilled from a small Claisen flask and yielded: (*c*) 2.5 g. of bluish distillate and (*d*) 10.1 g. of pale-greenish distillate (b.p. 65–85° at 2 mm.; m.p. 30–35°). The wax (*d*) was centrifuged at 0° and the almost colorless product was sublimed at the pressure of a mercury pump; the sublimate was pressed between filter paper, and the product was then reduced. The crude hydrochloride of the reduction product was extracted with tertiary amyl alcohol and gave 3.7 g. of the dihydrochloride of isoamylenediamine and 1.7 g. of syrupy product which was not identified. The benzoate prepared from the dihydrochloride did not depress the melting point of the benzoate prepared from the dihydrochloride of experiment 33.

[g] Isoamylene nitrosyl chloride (15.5 g.) was dissolved in 100 cc. of methyl alcohol, saturated with ammonia at 0°, and, after 1 hour, the solution was heated on a steam bath, while a stream of ammonia was bubbled into the solution. Solvent was distilled *in vacuo*, the residue was extracted with hot benzene, the insoluble product (*1*) was removed by filtration, solvent was distilled *in vacuo* from the filtrate, and left 3.8 g. of oil from which 2 g. of 2-methyl-2-aminobutanone-3 oxime (m.p. 103–104°; *Anal.* calc'd for $C_5H_{12}N_2O$: C, 51.68; H, 10.43; N, 24.12. Found: C, (*1*) 51.88; (*2*) 51.78; H, (*1*) 10.26; (*2*) 10.30; N, (*1*) 23.93; (*2*) 24.23) separated, yielding a dibenzoate, m.p. 146–147°, identical with that prepared from the oxime hydrochloride isolated from *1*.

Solid *1* was extracted with hot secondary butyl alcohol, the insoluble ammonium chloride (1.3 g.) was removed by filtration, and the filtrate yielded 11.8 g. of the oxime hydrochloride (*2*) (m.p., 192–193°: *Anal.* calc'd for $C_5H_{12}N_2O \cdot HCl$: Cl, 23.24. Found: Cl, 22.88). One gram of *2* gave 1.1 g. of crude dibenzoate, m.p. 136–138°, which melted at 146–147° after recrystallization from an alcohol-ether solution. (*Anal.* calc'd for $C_{19}H_{20}N_2O_3$: C, 70.45; H, 6.18; N, 8.64. Found: C, 70.33; H, 6.21; N, 8.96.) Small amounts of impurities, or possibly stereomeric products, were isolated in the purification of the oxime and its benzoate: the oily product isolated in the purification of the oxime yielded a benzoate, m.p. 145–146°, identical with that prepared from the crystalline oxime and that obtained from the hydrochloride (*2*).

Seven grams of *2*, dissolved in 150 cc. of ethyl alcohol, was reduced by gradually adding 2.5% amalgam (prepared from 620 g. of mercury and 15.5 g. of sodium) and 50 cc. of glacial acetic acid. Water was added to dissolve precipitated salts, the mercury was separated, the aqueous solution was acidified with gaseous HCl, the precipitated salt (*3*) was removed by filtration, and solvent was distilled *in vacuo* from the filtrate, leaving a solid residue (*4*). The combined solids (*3* and *4*) were extracted with hot ethyl alcohol; the insoluble sodium chloride (38.8 g.) was removed by filtration, solvent was distilled *in vacuo* from the filtrate, the syrupy residue was made alkaline, the mixture was distilled, the distillate was acidified with gaseous HCl and evaporated to dryness *in vacuo*. The residue was extracted with hot secondary butyl alcohol, the insoluble ammonium chloride (2.5 g.) was removed by filtration, solvent was distilled *in vacuo* from the filtrate, and left 4.6 g. of syrupy residue. The syrup was dissolved in hot, secondary butyl alcohol, the cooled solution was added to ether, and the precipitated gummy product, after a second treatment with hot secondary butyl alcohol, yielded 0.7 g. of the dihydrochloride of isoamylenediamine (P), which yielded the dibenzoate of isoamylenediamine (*Anal.* calc'd for $C_{19}H_{22}N_2O_2$; C, 73.55; H, 7.1; N, 9.04. Found: C, 73.63; H, 7.0; N, 9.21).

stirred one-half hour, solvent was distilled *in vacuo*, an ether solution of the residual oil was washed with water, and dried, and the solvent was removed. The blue residual oil (3 g.) deposited no solid; with a solution prepared from 0.9 g. of sodium, 25 cc. of methyl alcohol, and 4.1 g. of thiophenol, the blue oil gave 1.1 g. of sodium nitrite (Calc'd: Na, 33.3. Found: Na, 33.1), and 3.1 g. of oily product, which, after oxidation with hydrogen peroxide, gave: (*a*) 1.3 g. of impure solid, and (*b*) 1.4 g. of oily product. Oxidation of *b*, with chromic anhydride, gave 0.65 g. of 2-methyl-3-nitro-2-phenylsulfone butane; sublimation of *a* gave 1.1 g. of the pure sulfone.

(*b*) *With ozone.*—Ozone was bubbled, at 0°, into a suspension of 2 g. of the nitroso-nitro compound in 25 cc. of chloroform for one hour after the blue coloration was discharged (total time, 4 hours). Solvent was distilled *in vacuo*; the residue was dissolved in ether, and the solution was washed with water. The dried solution gave 2.3 g. of a waxy solid which, with a solution prepared from 0.6 g. of sodium, 25 cc. of methyl alcohol and 3.1 g. of thiophenol, gave 0.9 g. of sodium nitrite (calc'd: Na, 33.3; found: Na, 33.3) and 2.2 g. of crude, thio-ether, yielding, after oxidation with hydrogen peroxide, (*a*) 0.8 g. of impure solid, and (*b*) 1. g. of oily product. Oxidation of *b*, with chromic anhydride, gave 0.6 g. of 2-methyl-3-nitro-2-phenylsulfone butane: *a*, with 0.3 g. of chromic anhydride, gave 0.7 g. of the pure sulfone, m.p. 100–102°.

Experimental evidence for the formation of the nitrous ester of nitroisopentane.—Isolation of the nitro-nitrite has not been realized, but its appearance in the distilled blue product, formed by the action of nitrogen tetroxide upon trimethylethylene in ether solution, is manifested in the formation of ammonia and 2-methyl-3-aminobutanol-2 on reduction of the volatile blue oil. The yield of the amino alcohol, isolated as the benzoate, indicated that the nitro-nitrite constituted 9% of the crude addition product. However, quantitative isolation of the amino alcohol

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[h] Isoamylene nitrosyl chloride (21 g.), treated with alcoholic ammonia, as described above, yielded 1.4 g. of ammonium chloride, 4.5 g. of 2-methyl-2-aminobutanone-3 oxime, and 15 g. of the corresponding oxime hydrochloride (*1*).

Seven grams of *1*, dissolved in 25 cc. of methyl alcohol, was treated with excess gaseous HCl, solvent was distilled *in vacuo*, the residual dihydrochloride (7 g.) was dissolved in a mixture of 50 cc. of glacial acetic acid and 75 cc. of ethyl alcohol and reduced by gradually adding 2.5% amalgam (prepared from 620 g. of mercury and 15.5 g. of sodium). The product, isolated as described above, was converted to the dibenzoate; the dibenzoate did not depress the melting point of the dibenzoate prepared from the reduction product of experiment 31.

[i] Isoamylene nitrosyl chloride (6 g.), treated as above, yielded 0.4 g. of 2-methyl-2-aminobutanone-3 oxime and 5.9 g. of the corresponding oxime hydrochloride (*1*), m.p. 192°. A suspension of *1* in 50 cc. of glacial acetic acid, containing 0.9 g. of dissolved sodium, absorbed, with platinum oxide catalyst, only 290 cc. of hydrogen during 32 hours. Gaseous HCl was bubbled into the solution, catalyst and sodium chloride were removed by filtration, solvent was distilled *in vacuo*, and, from the residue, the dihydrochloride of *1* was extracted with hot secondary butyl alcohol. A solution of 2.5 g. of the recovered product in 25 cc. of ethyl alcohol, containing platinum oxide catalyst, absorbed only 20 cc. of hydrogen during 4 hours: the dihydrochloride of *1* was recovered.

A solution of 5.7 g. of the dihydrochloride of *1* was reduced, as before, with 2.5% amalgam (prepared from 500 g. of mercury and 12.5 g. of sodium) and the product was isolated as in experiment 35.

TABLE VI
REDUCTION PRODUCTS OF BLUE OILS

EXPT. NO.	LOW-PRESSURE DISTILLATION				BLUE OIL REDUCED				ETHER EXTRACT GAVE FRACTIONS:		
	Liquid, g.	Product from Expt. No.	Blue dist. (A), g.	Residual Oil (A), g.	g.	Solvent, cc.	Hydrogen absorbed lts.	Hydrogen absorbed hrs.	No.	g.	B.p., °C.
38[a]	20.6	19			20.6	75	11.7	25	*1*	1.2	Up to 145 (mainly 140–145)
									2	3.3	145–155 (mainly 145)
									3	1.7	Residual oil; b.p. 140–180 six months after prep'n
39[b]	11.6	20	27.2	21.7	27.2	50	17.01	57	*a*	Ether	34.5–35.3
	16.1	21							*1*	5.5	Up to 100
	22.8	22							*2*	0.6	100–145
									3	3.6	Residual oil
40[c]	19.1	24	29.5	31.0	20.8	50	12.7	66	*a*	Ether	34.7–35.4
	22.1	25							*1*	6.3	37–59 (mainly ether)
	22.4	26							*2*	1.1	59–92 (mainly 86–92)
									3	0.7	60–70 at 2 m.m.
									4	1.5	Tarry residue
41[d]	28.4	(a)	24.9	25.5	20.1	50	10.01	89	*a*	Ether	34–35.2
	24.6	(b)							*1*	1.1	50–100
									2	4.0	100–160
									3	0.5	Residual oil

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[a] Crude product 19 was reduced. During the distillation at low pressure, about one-half of the reduction product was lost by volatilizing through a condenser cooled to −25°. The residual oil (6.4 g.) gave fractions *1–3*. A portion (0.1 g.) of *3* with camphorsulfonic acid (0.5 g.) in hot acetic ester solution, gave 0.3 g. of the camphorsulfonate of isoamylenediamine, m.p. 263°; 0.1 g. of *2* gave 0.45 g. of the same salt (*Anal.* calc'd. for $C_{25}H_{44}N_2O_8S_2$: C, 53.25; H, 7.85; N, 4.95; S, 11.35. Found: C, 53.12; H, 8.30; N, 4.86). An identical salt was obtained from the reduction product of the dimeric nitroso-nitro derivative of isopentane: 1 g. of the bis derivative, in 25 cc. of glacial acetic acid containing platinum oxide catalyst, absorbed 790 cc. of hydrogen during 79 minutes. The product, isolated in the usual manner, was distilled *in vacuo* and, with a solution of camphorsulfonic acid in hot acetic ester solution, gave the camphorsulfonate of isoamylenediamine (m.p. 264°: *Anal.* Found: C, 53.14; H, 8.19; N, 4.91; S, 11.44).

A portion (0.3 g.) of *1* gave 0.4 g. of O, m.p. 147–148°: 1 g. of *2* gave 0.7 g. of O, m.p. 147–148°: 1 g. of *3* gave 0.4 g. of O, m.p. 147–148°, and a pasty, unidentified product.

[b] Distillate *a*, with gaseous HCl, gave 1.8 g. of P (crude product, m.p. 190–200; after crystallization from acetone, m.p. 209°). [Barrows and Ferguson (*J. Chem. Soc.*, **1937,** 114) have previously described the *p*-nitrobenzoate and the hydrochloride of 2-methyl-3-aminobutane.]

was not realized and the estimated concentration of the nitro-nitrite represents, therefore, the minimum value.

Nitrogen tetroxide (21.1 g.), distilled, during 70 minutes, into a mechanically stirred solution of 20 g. of trimethylethylene in 60 cc. of ether, cooled to −8°, yielded 2.7 g. of the dimeric nitroso-nitrate derivative of isopentane, m.p. 104°, and a liquid

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Refractionation of *1* gave: (*4*) 2.2 g., b.p. 34.5–36° (mainly ether), and (*5*) a residual oil which, combined with *2*, gave 1.8 g. of 2-methyl-3-aminobutane, b.p. 85–89°: 0.2 g. of the amine gave 0.5 g. of Q (m.p. 114–115°: *Anal.* calc'd for $C_{12}H_{16}N_2O_3$: C, 61.0; H, 6.8; N, 11.85. Found C, 61.14; H, 6.95; N, 11.63).

Residual oil *3*, at 2 mm., gave a colorless distillate *6*, 2.4 g., which, at ordinary pressure, yielded: (*7*) 1.7 g. of basic liquid (b.p., 152–162°; n_D^{20} 1.4454), leaving a residual oil (0.5 g.; n_D^{20} 1.4471). Distillate *7* gave only a trace of crystalline product with camphorsulfonic acid, and oily products with *p*-nitrobenzoyl chloride.

[c] The blue distillate A, refractionated at 2 mm., with the bath temperature gradually increased from 60° to 75° during 2 hours, gave: (*b*) 22.3 g. of blue distillate, and (*c*) 6.2 g. of green residual oil. During 15 hours *b* deposited 1.5 g. of the bis-nitroso-nitro derivative of isopentane. The blue filtrate (20.8 g.) was reduced.

Distillate *a* and *1*, with gaseous HCl, gave 0.8 g. of P, m.p. 208°: 0.5 g. of P gave 1.1 g. of crude Q which, after crystallization from ether, yielded 0.9 g. of pure Q, m.p. 114–115°.

A portion (0.5 g.) of *2* gave 0.8 g. of crude Q, m.p. 110°, which, after crystallization from an ether-petrol solution, melted at 113–114°.

[d] The crude addition products (*a* and *b*), prepared in the usual manner in an atmosphere of nitrogen, using 120 g. of technical arsenous oxide, 80 cc. of nitric acid (density 1.314), 20 g. of trimethylethylene and 60 cc. of ether, were distilled at low pressure. During 12 hours, the blue distillate (A) deposited 4.1 g. of the bis-nitroso-nitro derivative of isopentane: the blue filtrate (20.1 g.) was reduced. With gaseous HCl, the reduction products gave 1.4 g. of ammonium chloride and a syrupy product which, after extraction with ether, was made alkaline; the mixture was extracted with ether and the dried extract gave fractions *a*–*3*.

Gaseous HCl gave an inappreciable precipitate with *a*. A portion (0.3 g.) of *1* gave 0.4 g. of crude Q, which, after two recrystallizations from ether, yielded 0.1 g. of pure Q; m.p. 115°. With gaseous HCl, 0.65 g. of *1* gave 0.15 g. of P; 0.15 g. of P gave 0.3 g. of crude Q, from which 0.1 g. of pure Q, m.p. 114–115°, was isolated.

One gram of *2*, with benzoyl chloride, gave 1.2 g. of oily product which yielded 0.25 g. of O, m.p. 146–148°. A solution of 3 g. of *2* in 25 cc. of ether gave, with gaseous HCl, a syrup, which, boiled with secondary butyl alcohol, yielded 1.2 g. of the dihydrochloride of isoamylenediamine (*4*) (0.5 g. of the salt gave 0.8 g. of crude O, from which 0.6 g. of pure O, m.p. 146–147°, was isolated) and (*5*) a syrup (3.5 g.) which could not be crystallized.

The syrupy product (*5*) was made alkaline, using 8 g. of KOH and 25 cc. of water, and the mixture was warmed with 7 g. of benzoyl chloride. The oily product (3.9 g.), at the pressure of a mercury pump, gave: (*6*) 2.2 g. of pale-yellow, viscous distillate, and (*7*) 1 g. of residual oil which yielded 0.2 g. of O, m.p. 147–148°, and products that could not be purified. Distillate *6*, dissolved in 20 cc. of ether, gave, with gaseous HCl, a clear solution from which petrol precipitated an oil. This oil was only partly soluble in water; the mixture was made alkaline, and the liberated impure benzoate of 2-methyl-3-aminobutane was redistilled at the pressure of a mercury pump. The crude distillate was analyzed. (*Anal.* calc'd for $C_{12}H_{17}NO$: C, 75.7; H, 8.42; N, 7.36; found C, 74.39; H, 8.98; N, 8.13.)

product (35.3 g.) which, on distillation at low pressure, yielded: (*a*) 14.9 g. of blue distillate, and (*b*) 19.2 g. of green, residual oil. Oil *a* was fractionated at 2 mm., and gave: (*c*) 7.6 g. of blue distillate, and (*d*) 5.7 g. of bluish-green residual oil, which was distilled in an all-glass apparatus and gave a distillate of 5.2 g. (*e*).

A solution of 6.6 g. of *c* in 25 cc. of glacial acetic acid, containing platinum oxide catalyst, absorbed 4.3 l. of hydrogen during 89 hours. Catalyst was removed by filtration, gaseous hydrogen chloride was bubbled into the filtrate, the precipitated ammonium chloride (0.5 g.) was removed by filtration, solvent was distilled from the filtrate, *in vacuo*, and the residual syrup was made alkaline. The mixture was extracted with ether, and the dried ether solution, on fractionation, yielded: (*1*) an ether distillate, b.p. 34.5–35°, and (*2*) 1.7 g. of basic oil, b.p. 120–180° (nearly all at 160–165°). Distillate *1* gave, with gaseous hydrogen chloride, 0.5 g. of crystalline hydrochloride which, with 0.8 g. of *p*-nitrobenzoyl chloride, gave 1.2 g. of crude product, m.p. 110–112°, from which, after extraction with hot sodium carbonate solution and recrystallization of the product from ether solution, the pure *p*-nitrobenzoate of 2-methyl-3-aminobutane, m.p. 114°, was isolated.

Benzoylation of 1 g. of *2* gave 1.8 g. of oily product which, distilled at the pressure of a mercury pump and with the bath temperature at 180°, yielded (*3*) 1.4 g. of a viscous distillate, and (*4*) 0.4 g. of residual oil, from which 0.05 g. of isoamylenediamine dibenzoate, m.p. 145–146°, was isolated. An ether solution of *3* deposited 0.8 g. of impure benzoate of 2-methyl-3-aminobutanol-2, m.p. 85–90°, which, after recrystallization from ether, melted at 90–92° and did not depress the melting point of a specimen of the pure benzoate.

A solution of *e* in 25 cc. of glacial acetic acid, containing platinum oxide catalyst, absorbed 3.9 l. of hydrogen during 103 hours. Catalyst was filtered off, gaseous hydrogen chloride was bubbled into the filtrate and, since no precipitate was formed, the solvent was distilled *in vacuo*. The residual syrup, dissolved in hot secondary butyl alcohol, deposited 1 g. of the dihydrochloride of isoamylenediamine (*f*). One-half gram of *f* gave 0.5 g. of pure, recrystallized dibenzoate of isoamylenediamine, m.p. 147–148°: 0.5 g. of *f* gave 1 g. of crude *p*-nitrodibenzoate of isoamylenediamine, from which, after extraction with hot sodium carbonate solution and recrystallization of the product from acetone, 0.7 g. of pure *p*-nitrodibenzoate (m.p. 229°. *Anal.* calc'd for $C_{19}H_{20}N_4O_6$; C, 57.0; H, 5.0; N, 14.0; found C, 57.0; H, 5.09; N, 14.07) was obtained. The filtrate yielded a syrup, which was made alkaline and the mixture extracted with ether. The dried, ether solution was fractionated, and gave: (*5*) an ether distillate (b.p., 35–36°; with gaseous hydrogen chloride, and inappreciable yield of salt was formed), and (*6*) 3.5 g. of basic oil, b.p., 120–160° (mostly at 155–160°).

With *p*-nitrobenzoyl chloride, 0.3 g. of *6* gave 0.8 g. of oily product; with camphorsulfonic acid, 0.3 g. of *6* gave 0.1 g. of crystalline product, which could not be purified, and with benzoyl chloride (0.5 g.), 0.7 g. of oily product was obtained from which 0.1 g. of the benzoate of 2-methyl-3-aminobutanol-2, m.p. 92°, was isolated. Benzoylation of 2 g. of *6* yielded 3.3 g. of viscous oil, which was distilled, at the pressure of a mercury pump, with the bath-temperature at 180° gave: (*7*) 2.5 g. of a viscous distillate, and (*8*) 0.4 g. of residual oil, which, dissolved in ether, yielded 0.25 g. of the dibenzoate of isoamylenediamine, m.p. 146–147°. Distillate 7 solidified completely; on fractional crystallization, it yielded the benzoate of 2-methyl-3-aminobutanol-2 [the three fractions of crystals: (*a*) 0.7 g., m.p. 93°; (*b*) 0.6 g., m.p. 92–93°, and (*c*) 0.2 g., m.p. 90° were slightly impure, but it did not depress the melting point of a pure specimen of the benzoate of the amino alcohol], and an oily product

(*9*, 1 g.) which contained approximately equal amounts of the benzoate of 2-methyl-3-aminobutanol-2 and the dibenzoate of isoamylenediamine, and could not be crystallized. Redistillation of *9* yielded: (*10*) 0.4 g. of distillate, and (*11*) 0.4 g. of residual oil. An ether solution of *10* yielded 0.2 g. of the benzoate of 2-methyl-3-aminobutanol-2, m.p. 91–92°, and *11* yielded 0.15 g. of the dibenzoate of isoamylenediamine, m.p. 146–147°.

SUMMARY

1. The action of "nitrous fumes" upon trimethylethylene has been re-investigated. Schmidt, with "nitrous fumes", generated from nitric acid of density 1.43, obtained 55–66 per cent. yields of a solid product, assumed to be the dimeric nitrous ester of 2-methyl-3-nitrosobutanol-2. We obtained, under comparable conditions, the corresponding dimeric nitric ester, and the main product, a greenish-blue oil, deposited no solid during two weeks. It is shown that the solid nitrogen trioxide addition product is not the dimeric, nitroso-nitrite compound, but is the corresponding nitroso-nitro derivative, which, with "nitrous fumes", or with ozone, is oxidized to 2,3-dinitro-2-methylbutane, and is catalytically reduced to isoamylenediamine.

2. Precautions were taken to treat the arsenous oxide and nitric acid mixtures uniformly; yet, because of variable behavior, the results could not be reproduced quantitatively. The variations in the results obtained with nitric acid of density 1.41 were most marked. At −10°, the product yielded 4.5 per cent. of the dimeric nitric ester of 2-methyl-3-nitrosobutanol-2, but the corresponding bis-nitroso-nitro derivative separated in yields of 9.4 and 3.4 per cent., respectively, from the products formed at 4° and 7°. The results obtained with moist "nitrous fumes" were no more consistent in nitrogen than in air, and equally discordant results were obtained in experiments made under anhydrous conditions.

3. The yield of dimeric 3-nitroso-2-nitro-2-methylbutane, produced with nitric acid (density 1.30–1.312) yielding an excess of nitric oxide, varied from 8.6 to 17.4 per cent. Under anhydrous conditions and in an atmosphere of nitrogen, conditions seemingly more favorable for the formation of derivatives of nitrogen trioxide than those described by Schmidt, the bis-nitroso-nitro derivative was obtained in a maximum yield of 20 per cent., and under no conditions could Schmidt's high yields (55–66 per cent.) be duplicated.

4. At −80°, products were formed which decomposed, below 0°, with evolution of gas, and it is suggested that the inconsistent yields of the addition products may be attributed to a primary formation of a reaction product that undergoes spontaneous decomposition to yield the isolated products.

5. The liquid reaction products were separated by low-pressure distil-

lation into an easily volatile blue and a much less volatile, green oil, from which a small amount of 2,3-dinitro-2-methylbutane was isolated. Indirect determinations showed that the dinitro compound constituted 10–20 per cent. of the crude reaction product, but, since the method gives low results, the actual concentration is probably higher. Undoubtedly the dinitro compound is formed mainly by direct addition of nitrogen tetroxide to the alkene, although the compound may also be formed by oxidation of the corresponding nitroso-nitro derivative of isopentane. Accordingly, the yield of the dinitro derivative probably varied with the experimental conditions and with the composition of the "nitrous fumes", but a correlation is not apparent from our results. Beside the dinitro compound, oils of high molecular weight (213–360) appeared in the non-volatile green oils. The chemical nature of these viscous liquids, constituting 10–20 per cent. of the reaction product, could not be established, but the formation may be attributed to the action of "nitrous fumes" upon polymers of trimethylethylene, which are formed rapidly by the action of acidic reagents upon the alkene.

6. From the volatile blue oils, dimeric 3-nitroso-2-nitro-2-methylbutane separated in varying yields. The residual oils, after fractionation, gave values on analysis closely approaching those calculated for 2-methyl-3-nitrobutene-2 and, from the analytical data, it is estimated that the nitroalkene constituted 10–20 per cent. of the reaction product. The presence of the nitroalkene was established by (1) conversion to 2-methyl-3-nitro-2-phenylsulfone butane, and (2) by reduction to the corresponding amine. The nitroalkene appears, not only in the products formed from "nitrous fumes", but, also, in those obtained with nitrogen tetroxide. The suggestion is made that a primarily formed addition product undergoes spontaneous decomposition to yield the nitroalkene.

7. Previous work has shown that reduction with metal and acid removes most of the nitrogen from the addition products formed with nitrogen trioxide and tetroxide. Catalytic reduction, however, reduces the addition compounds without severing the nitrogen from carbon; the dimeric nitric ester of 2-methyl-3-nitrosobutanol-2 yielded ammonia and 2-methyl-3-aminobutanol-2, the dimeric nitroso-nitro, and the dinitro, derivative of isopentane yielded isoamylenediamine. These results confirm the structure of the nitroso-nitrate and establish the structures of the nitroso-nitro and the dinitro derivative, which was previously formulated as the nitro-nitrite because of the facile and quantitative conversion, with sodium thiophenylate, to the corresponding sulfone, 2-methyl-3-nitro-2-phenylsulfone butane.

8. Reduction of the crude and the fractionated blue oils gave mixtures of amines which were difficult to separate. The easily volatile amine,

2-methyl-3-aminobutane, formed from 2-methyl-3-nitrobutene-2, was readily isolated and identified through the *p*-nitrobenzoate, but the higher-boiling amines yielded oily acylation products from which only the derivatives of isoamylenediamine could be isolated. It is suggested that the oily acylation products were mainly derived from 2-methyl-3-aminobutanol-2.

9. Reduction of the volatile blue oil, formed by the action of nitrogen tetroxide upon trimethylethylene in ether solution, gave ammonia, 2-methyl-3-aminobutanol-2 and isoamylenediamine. The appearance of ammonia and the amino alcohol in these products leads to the conclusion that the nitro-nitrite derivative of isopentane is formed in the addition of nitrogen tetroxide to trimethylethylene. A corresponding nitroso-nitrite derivative may appear in the products formed by the action of "nitrous fumes" upon the alkene, but our results do not definitely prove that a derivative of the trioxide, in which a nitrogen atom is attached to carbon through oxygen, is formed.