Table VIII

N.m.r. Analysis of Norbornylene Adduct

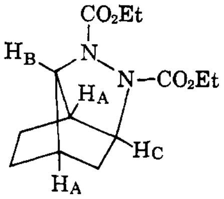
	Analysis, %		δ,
	Calcd.	Found	p.p.m. from TMS
CH_3 + ring hydrogens	12	12	1.28 (center line)
H_A	2	2.3	2.45
H_B or H_C	1	0.9	3.66 or 4.35
OCH_2 + H_B or H_C	5	4.8	4.09, 4.13

crude product indicated four components. The major component was eluted first on an acid-washed alumina column with methylene chloride as eluent. This compound (90% pure) was rechromatographed in the same manner to 95% purity (v.p.c.) and showed no N–H absorption according to infrared analysis. Of the other three minor components, one corresponded to ethyl hydrazodicarboxylate and the other two were not identified.

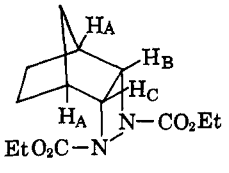
Anal. Calcd. for $C_{13}H_{20}N_2O_4$: C, 58.15; H, 7.51. Found: C, 58.32; H, 7.68.

N.m.r. was consistent with the structure **23** (see Table VIII). A cycloaddition product such as **24** would also be compatible with the observed n.m.r. if inversion of the carbethoxyl group were restricted. It is, however, likely that the inversion of these groups would be sufficiently free such that the bridgehead hydrogens would be equivalent and give a different n.m.r. spectrum from that observed.

Reaction with N-Benzylidenebutylamine.—N-Benzylidenebutylamine ($C_6H_5CH{=}NCH_2CH_2CH_2CH_3$) was prepared by azeotropic distillation of a benzene solution of *n*-butylamine and benzaldehyde (83.5% yield), b.p. 52–54° (0.2 mm.).



23



24

A sample of 16.1 g. of this imine (0.1 mole) and 4.33 g. (0.025 mole) of ethyl azodicarboxylate was placed in a 50-ml. bomb tube and heated for 45 hr. at 80°. The reaction mixture was then distilled at reduced pressure and 13.2 g. of unreacted imine recovered. The nonvolatile residue (6.2 g.) was a rather immobile liquid which was glassy when cold.

Anal. Calcd. for $C_{23}H_{35}O_8N_5$: C, 54.21; H, 6.92; N, 13.75; mol. wt., 509.6. Found: C, 53.90; H, 6.94; N, 13.86; mol. wt., 465. The analysis indicated the formation of a 2:1 azo ester–imine adduct in 97.7% yield. The n.m.r. of this product was consistent with structure **21**.

The ultraviolet spectrum of an acetonitrile solution showed a maximum at 244 mμ (ε 9410) as did the N-benzylidenebutylamine (ε 9075).

Acknowledgment—The authors wish to thank Messrs. J. J. Werner and J. H. Surridge for their very competent technical assistance.

The Reactions of Nitric Oxide with Tri- and Tetramethylethylene. The β-Nitroolefin and Nitrosite Rearrangements

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When the branched olefins trimethylethylene and tetramethylethylene were treated with nitric oxide at room temperature, reaction occurred smoothly to produce mixtures of nitroolefins (mainly) along with lesser quantities of nitrosites, dinitroalkanes, nitro alcohols, and cleavage products. The structures of most of the nitrated products were found to be analogous to those of the corresponding products derived from isobutylene or the unbranched olefins; *i.e.*, the nitro groups appeared at the less heavily substituted of the original olefinic carbons, and the other substituents or double bond termini appeared at the more heavily substituted position. In addition to these "normal" nitration products, "abnormal" allylic isomers of the β-nitroolefins appeared in considerable quantity, *e.g.*, 2-methyl-1-nitro-2-butene from trimethylethylene and 2,3-dimethyl-1-nitro-2-butene from tetramethylethylene. It was found that these arose from a remarkably facile, NO_2-catalyzed allylic rearrangement of the normal products, 2-methyl-3-nitro-1-butene and 2,3-dimethyl-3-nitro-1-butene, respectively. This rearrangement is believed to result from the addition of NO_2 to the β-nitroolefin to give a β,β′-dinitroalkyl radical which can then lose either β-nitro group to form either β-nitroolefin. It is suggested that similar eliminations of nitro groups from β-nitroalkyl radicals are also responsible for the thermal regeneration of olefins from certain nitrosites, the low kinetic chain lengths of nitroalkane chlorinations, and the very well-known NO_2-catalyzed *cis–trans* isomerization of olefins. It was long assumed that trimethylethylene nitrosite had an "abnormal" structure (secondary nitroso group, tertiary nitro) because upon treatment with alkalis or amines it yielded ketoximes, often with additional displacement of the nitro group by –OH, –NHR, etc. The present study confirmed the ketoxime formation, but showed that the original nitrosite actually had the "normal" structure (secondary nitro, tertiary nitroso) as required by the nitration mechanism. An intramolecular oxygen shift ("nitrosite rearrangement") is proposed in order to account for the ketoxime formation.

Most olefins react readily with nitric oxide containing catalytic traces of NO_2, thereby producing α- and β-nitroolefins, nitrosites, and a variety of other nitrated products. In the case of isobutylene, these products have been studied in detail and a mechanism proposed to account for the observed reaction behavior.[1] In this paper, we shall describe the products obtained from tri- and tetramethylethylene, and shall discuss two new rearrangements which were encountered during the course of these studies.

Experimental

Nitration of Trimethylethylene.—The olefin (385.5 g., 5.50 moles) was charged into a 1-l. Parr reactor fitted with a stirrer, cooling coils, and collection tank for the product gases, and flushed with dry nitrogen. Nitric oxide (205.5 g., 6.85 moles) under 50-p.s.i.g. pressure was added at a rate of 4.5 moles/hr. at 21°. The deep green liquid reaction product was subjected to a flash distillation in a falling film evaporator at 100° at 1 mm., and then further fractionated and analyzed by the general procedures[1] used for the isobutylene–nitric oxide reaction products. The indicated product composition is shown in Table I.

During the distillations, there was a considerable conversion of the nitrosite (VI) and presumably also of any N-(2-methyl-3-nitro-2-butyl)hydroxylamine present to regenerated trimethyl-

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[1] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **79**, 2480 (1957).

TABLE I

COMPOUNDS IDENTIFIED IN THE REACTION PRODUCT OF TRIMETHYLETHYLENE AND NITRIC OXIDE

Product	Yield, mole(s)	Estimated net yield, %
2-Methyl-3-nitro-1-butene (I)	0.50	24.6
2-Methyl-1-nitro-2-butene (II)	0.46	22.7
2-Methyl-3-nitro-2-butene (III)	0.44	21.7
2-Methyl-3-nitro-2-butanol (IV)	0.13	5.9
2-Methyl-2-nitro-2-butyl nitrate (V)	0.02	1.0
2-Methyl-3-nitro-2-nitrosobutane[a] (VI)	0.006	0.3
2,3-Dinitro-2-methylbutane (VII)	0.03	1.5
Acetaldehyde	0.01	0.0
Acetone	0.001	0.05
Methyl isopropyl ketone	0.01	0.5
Acetic acid	0.02	1.0
Nitromethane	0.02	1.0
Unidentified carbonyl compounds	0.02	1.0
Unidentified nitrile	Trace	0.0
Distillation residues[b] (VIII)	0.35	17.3
Recovered trimethylethylene	2.02	
Unrecovered and regenerated trimethylethylene (estimated)[c]	1.45	
N_2 generated during reaction	1.56	
Water	0.78	
Nitric oxide unreacted	0.06	
Nitric oxide regenerated (estimated)[c]	1.66	
Handling loss of stable products[b] (estimated)[c]	0.03	

[a] Isolated as crystalline dimer. [b] For purposes of calculation, assumed to have the composition $(C_5H_9NO_2)_x$. [c] These estimates lead to material balances in C, H, N, and O between the reactants and products.

ethylene and nitric oxide. The recovered yield of nitrosite was nil from a large-scale distillation and 4.6% from a small-scale distillation; the initial yield of nitrosite in the deep green crude product was undoubtedly greater still. Because of this tendency for certain products to revert to the starting materials,[1] and because our work-up procedure did not clearly distinguish unreacted from regenerated trimethylethylene, it was not possible to determine precisely how much trimethylethylene actually entered into the reaction. Hence, true yields of the various products obtained, based upon trimethylethylene undergoing reaction, could not be calculated. Accordingly, in Table I are reported the true molar conversions observed and the estimated net yields, *i.e.*, yields based upon the trimethylethylene which underwent reaction but was not subsequently regenerated.

2-Methyl-2-nitro-1-butene (I).—Redistillation of a crude fraction boiling at 53.5–56° (19 mm.) in a Piros-Glover spinning band column gave 2-methyl-3-nitro-1-butene, b.p. 56.5° (23 mm.), d^{20}_4 1.4352, d^{20}_4 0.982, M$_D$ 30.60. The infrared spectrum showed the characteristic bands[2] of the unconjugated nitro group at 6.47 and 7.32 μ, and the C=CH$_2$ group at 3.25, 6.04, and 10.93 μ.

Anal. Calcd. for $C_5H_9NO_2$: C, 52.2; H, 7.9; N, 12.2. Found: C, 52.6; H, 7.8; N, 12.2.

2-Methyl-1-nitro-2-butene (II).—This compound was also isolated from the crude fraction boiling at 53.5–56.5° (19 mm.) by redistillation in the Piros-Glover spinning band column; b.p. 72.5° (23 mm.), n^{20}_D 1.4475, d^{20}_4 0.995, M$_D$ 30.94. Upon ozonolysis acetaldehyde was obtained. The infrared spectrum showed unconjugated nitro group bands at 6.42 and 7.26 μ and a trisubstituted ethylene C–H wagging band at 11.88 μ.

Anal. Calcd. for $C_5H_9NO_2$: C, 52.2; H, 7.9; N, 12.2. Found: C, 52.6; H, 8.2: N, 12.6.

The compound was also obtained by the procedure which was originally reported to yield 2-methyl-1-nitro-1-butene.[3] A mixture of 50 ml. of butanone, 50 ml. of nitromethane, and 5 ml. of piperidine was allowed to stand 6 days at 25–30°, and then acidified and distilled to give 3.0 g. of the nitroolefin, a colorless liquid having a mild odor, b.p. 56.5–57.5° (9.5 mm.); 2 g. of 2-methyl-1-nitro-2-butanol, b.p. 86–87° (10 mm.); and 13 g. of 2-methyl-1-nitro-2-(nitromethyl)butane, b.p. 126–127° (4 mm.). The infrared spectrum of the nitroolefin agreed with that of the trimethylethylene nitration product, and was very different from that[2] of the conjugated isomer, 2-methyl-1-nitro-1-butene, which is a yellow lachrymatory oil. Presumably, the conjugated nitroolefin was formed first, and then reacted, in part with nitromethane to yield the dinitrohexane, and in part with the piperidine to yield the salt of the nitroolefin anion. The acidification of this allylic anion was observed in a separate experiment to effect protonation almost exclusively on the carbon α to the nitro group.

$$CH_3CH_2C(Me){=}CHNO_2 + C_5H_{11}N \longrightarrow CH_3CH{=}C(Me)CHNO_2^- + C_5H_{12}N^+$$

$$CH_3CH{=}C(Me)CHNO_2^- + H^+ \longrightarrow CH_3CH{=}C(Me)CH_2NO_2$$

2-Methyl-3-nitro-2-butene (III).—It was not possible to isolate this compound in a pure state by a fractional distillation, since its boiling point was almost identical with that of 2-methyl-1-nitro-2-butene. However, by washing the crude fraction, b.p. 66° (19 mm.), with aqueous caustic it was possible to achieve separation. The alkali-insoluble product was dried and distilled, giving pure 2-methyl-3-nitro-2-butene, b.p. 69.2° (20 mm.), n^{20}_D 1.4618, d^{20}_4 1.006, M$_D$ 31.45. The infrared spectrum indicated the presence of a conjugated nitro group (6.62 and 7.46 μ), and an olefinic double bond (6.01 μ), but no olefinic C–H bond.

Anal. Calcd. for $C_5H_9NO_2$: C, 52.2; H, 7.9; N, 12.2. Found C, 51.9; H, 7.4; N, 12.4.

2-Methyl-3-nitro-2-nitrosobutane Dimer (VI).—This compound separated as a white crystalline solid from the deep blue distillates that boiled over the range of 66–67.1° at 10 mm. or 46.0–46.5° at 1 mm. Its melting point was extremely dependent upon the rate of heating, *i.e.*, 69–71.5° at 3°/min., 80–82° at 9°/min. The melt was deep blue liquid, indicating the presence of a tertiary nitroso group in the monomer. The infrared spectrum showed the 6.44-μ band of a secondary nitro, but not the highly characteristic bands[2] of $-C(CH_3)_2NO_2$ or secondary bisnitroso groups.

Anal. Calcd. for $C_{10}H_{20}N_4O_6$: N, 19.2. Found: N, 18.8.

In order to replace the nitroso group by acetoxy, the dimeric nitrosite (0.19 g.) was added to 1 ml. of acetic anhydride containing a few milligrams of sulfuric acid at room temperature. The nitrosite reacted immediately with effervescence, but a faint blue color persisted for several minutes. The excess anhydride was pumped off; the residue washed was with alkali and dried to give 0.09 g. 2-methyl-3-nitro-2-butyl acetate, which had an infrared spectrum identical to that of an authentic specimen (colorless liquid, n^{20}_D 1.4356, or solid, m.p. 32°) prepared by the acetylation of 2-methyl-3-nitro-2-butanol.[3]

Nitration of Tetramethylethylene.—Nitric oxide (262 g., 8.75 moles) was added under 50-p.s.i.g. pressure at a rate of 4.8 moles/hr. to 421 g. (5.0 moles) of tetramethylethylene at 24° in the apparatus described above. The reaction product was chilled in an acetone–Dry Ice bath and filtered to remove the major part of the 2,3-dimethyl-2,3-dinitrobutane; the filtrate was subjected to flash distillation at 1 mm. and 100°. Further fractionation and analysis indicated the product composition shown in Table II.

As with the nitric oxide–isobutylene reaction product,[1] there were indications that very considerable changes in composition occurred during the product fractionation. First, the vacuum distillations and redistillations of the crude products were accompanied by very marked weight losses, indicating the formation of substances not condensible at −78° during the distillations. Second, there was a gradual loss in blue color and deposition of XI throughout the fractionation procedure, indicating the autoxidation and disproportionation of XII to XI. Third, infrared spectra of the first distillates indicated that they contained a considerable quantity (possibly 20% of the total crude product) of a nitrate ester, probably 2,3-dimethyl-2-nitro-3-butyl nitrate (XVII). This substances was virtually absent from the fractionated product; presumably it underwent disproportionation during the distillation. Therefore, Table II must also be regarded as indicative only of the distribution of readily isolatable or thermally stable products obtained from the tetramethylethylene–nitric oxide reaction, rather than a listing of the substances originally formed in the reaction.

2,3-Dimethyl-3-nitro-1-butene (IX).—This compound was isolated from a crude fraction boiling at 36–56° (10 mm.) by redistillation in the spinning band column; b.p. 55.1° (10 mm.), n^{20}_D 1.4420, d^{20}_4 0.973, M$_D$ 35.12. The infrared spectrum showed

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[2] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

[3] A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).

TABLE II

COMPOUNDS IDENTIFIED IN THE REACTION PRODUCT OF TETRAMETHYLETHYLENE AND NITRIC OXIDE

Product	Yield, mole(s)	Estimated net yield, %
2,3-Dimethyl-3-nitro-1-butene (IX)	0.42	14.8
2,3-Dimethyl-1-nitro-2-butene (X)	0.53	18.7
2,3-Dimethyl-2,3-dinitrobutane (XI)	0.79	27.9
2,3-Dimethyl-2-nitro-3-nitrosobutane[a] (XII)	0.48	17.0
2,3-Dimethyl-1-buten-3-ol (XIII)	0.23	8.1
2-Nitropropane	Trace	0.
Acetone (XIV)	0.27	9.5
Pinacol[b] (XV)	Trace	0[b]
Pinacolone (XVI)	0.005	
Distillation residues[c, d] (XVIII)	0.18	6.4
Recovered tetramethylethylene	0.70	
Unrecovered and regenerated tetramethylethylene (estimated)[e]	1.47	
Nitrogen generated during reaction	2.47	
Water	1.31	
Nitric oxide, unreacted	0.05	
Nitrogen generated in work-up (estimated)[e]	0.04	
Handling loss of stable products[c] (estimated)[e]	0.03	

[a] Isolated as crystalline 1:1 adduct with XI. [b] In a preliminary study of the reaction between tetramethylethylene and nitric oxide in carbon tetrachloride solution, the yield of pinacol (m.p. 41–42°; identified by infrared spectrum) rose to 5%. [c] For purposes of calculation, arbitrarily assumed to have the composition $(C_6H_{11}NO_2)_x$. [d] These residues contained traces of an unidentified nitrile and a nitrate ester XVII, believed to be 2,3-dimethyl-2-nitro-3-butyl nitrate. [e] These estimates lead to material balances between the reactants and products in C, H, N, and O.

the bands of a $C{=}CH_2$ group (3.25 and 6.00 μ) and a tertiary nitro group (6.49, 7.21, 7.24, 7.33, and 11.81 μ).

Anal. Calcd. for $C_6H_{11}NO_2$: C, 55.8; H, 8.6; N, 10.9. Found: C, 56.7, 56.2; H, 8.6, 8.5; N, 11.0.

2,3-Dimethyl-1-nitro-2-butene (X).—This compound was obtained by redistillation of the crude fraction boiling at 57.8–59° (5 mm.); b.p. 70.8° (10 mm.), 58.5–59.8° (5 mm.), $n^{20}\text{D}$ 1.4564, d^{20}_4 0.987, $M\text{D}$ 35.57. The infrared spectrum showed the bands of a primary nitro group (6.44, and 7.30 μ) and a tetrasubstituted ethylene (6.00 μ). Ozonolysis followed by decomposition of the ozonide over zinc dust gave acetone 2,4-dinitrophenylhydrazone, m.p. 126°.

Anal. Calcd. for $C_6H_{11}NO_2$: C, 55.8; H, 8.6; N, 10.9. Found: C, 55.6; H, 8.2; N, 11.0.

2,3-Dimethyl-2-nitro-3-nitrosobutane (XII).—This substance, although a major reaction product, could not be obtained free of 2,3-dimethyl-2,3-dinitrobutane, since it was not stable enough for distillation and apparently cocrystallized with the dinitro compound to form a deep blue 1:1 adduct. Upon oxidation of this adduct with air or oxygen 2,3-dimethyl-2,3-dinitrobutane was obtained quantitatively. The infrared spectrum showed the characteristic bands of tertiary nitro groups at 6.47 and 7.44 μ, but no band indicative of olefinic, oximino, or nitrate ester groups.

Anal. Calcd. for $C_6H_{12}N_2O_2 \cdot C_6H_{12}N_2O_4$: C, 42.8; H, 7.2; N, 16.7. Found: C, 42.8; H, 6.9; N, 17.2.

Isomerization of 2,3-Dimethyl-3-nitro-1-butene.—A solution of 0.2 g. of nitrogen dioxide in 2 ml. carbon tetrachloride was added to 1.9 g. of 2,3-dimethyl-3-nitro-1-butene in 20 ml. of carbon tetrachloride over a period of 0.7 hr. at 50°. The nitrogen dioxide decolorized only slowly, either by reaction or evaporation, indicating that it was present throughout this period. The solution was then extracted with water and distilled to give a small forerun followed by 0.95 ml. of dimethylnitrobutenes, b.p. 69.5° (10 mm.), $n^{20}\text{D}$ 1.4560. The infrared spectrum of this fraction and that of the forerun indicated an over-all composition of 91% 2,3-dimethyl-1-nitro-2-butene and 9% 2,3-dimethyl-3-nitro-1-butene. The kinetics of the isomerization were examined by adding a trace of nitrogen dioxide to the nitroolefin and observing the change in refractive index. It was found that the same final index was observed regardless of whether 2,3-dimethyl-1-nitro-2-butene ($n^{20}\text{D}$ 1.4564) or 2,3-dimethyl-3-nitro-1-butene ($n^{20}\text{D}$ 1.4420) was isomerized with the nitrogen dioxide. From the initial rates of change of refractive index in runs where the initial dinitrogen tetroxide concentrations were 0.45 and 1.0 M it was estimated that the isomerization was 0.6 order in dinitrogen tetroxide or approximately first order in nitrogen dioxide. Simple pseudo-first-order kinetics were not followed by the isomerization, however, since the dinitrogen tetroxide catalyst was slowly consumed by addition reactions, and an unidentified high boiling adduct or substitution product ($n^{20}\text{D}$ 1.4905) was formed.

The Reaction of 2-Methyl-3-nitro-2-nitrosobutene with Alkali.—One gram (0.007 mole) of trimethylethylene nitrosite dimer was warmed to 110° to convert it to the blue monomer and then cooled and stirred with 10 ml. of 1 N sodium hydroxide solution (0.010 mole) for several minutes at room temperature. It failed to remain monomeric, however, and soon set up to a semisolid mass. To promote reaction, 2 ml. of methanol was added and the mixture stirred at 50–60° until the blue color disappeared. The reaction product, a very pale yellow, turbid solution, was cooled and extracted with ether to remove 0.3 g. (0.003 mole) of crude oxime ether polymer. The alkaline aqueous solution was acidified with 1 N sulfuric acid, and extracted with ether to give 0.040 g. of crude methoxy oxime, m.p. 79–87°.

The methoxy oxime, 3-methyl-3-methoxy-2-butanone oxime, was recrystallized from $CHCl_3$–CCl_4; m.p. and m.m.p. 89–90°, lit.[4] 92–93°. Its infrared spectrum (Nujol mull) showed characteristic ketoxime bands at 2.98, 6.07, and 10.69 μ.

Anal. Calcd. for $C_6H_{13}NO_2$: N, 10.7. Found: N, 10.8.

The oxime ether polymer was a rather viscous, almost colorless, nonvolatile, thermally stable oil, $n^{20}\text{D}$ 1.4723. Its infrared spectrum indicated the absence of more than traces of nitro groups, but the bands of oxime (3.01, 6.1, and 1.06 μ) and ether (8.63 μ) groups were prominent and a general structural similarity to the methoxy oxime was evident. Accordingly, the substance was regarded as an oxime ether polymer, $H[ON{=}C(CH_3)C(CH_3)_2]_xOH$; the analysis was in best agreement with theory for $x = 3$.

Anal. Calcd. for $C_{15}H_{29}N_3O_4$: C, 57.2; H, 9.3; N, 13.3. Found: C, 56.7; H, 8.8; N, 13.9.

Nitrations in Polar Media.—In order to examine the effect of solvent polarity upon the nitration product distributions, the reactions of nitric oxide with trimethylethylene and tetramethylethylene vapors at 24° were studied briefly. It was established that the locus of reaction in such systems was the liquid layer of highly polar nitration products on the walls of the glass bulbs used; the reactions showed induction periods unless the walls were wet with the products of a previous run or with an inert solvent. A run in which 3 mmoles of trimethylethylene was consumed gave 0.1 mmole of ketones, 0.3 mmole of 2-methyl-3-nitro-2-butyl nitrate, 0.4 mmole of other nitrates, 1.9 mmoles of unconjugated nitro compounds, presumably mainly I and II, and 0.1 mmole of the conjugated nitro compound III. Similarly, a run in which 1.0 mmole of tetramethylethylene was consumed gave about 0.1 mmole of ketones, 0.2 mmole of the nitrate XVII, 0.5–0.6 mmole of the distillable nitroolefins IX and X, and about 0.1 of the dinitro compound XI. All of these products were identified by their infrared spectra.

Discussion

The Reactions of Nitric Oxide with Tri- and Tetramethylethylene.—The results show that the nitrations of tri- and tetramethylethylene with nitric oxide are fundamentally similar to those of isobutylene.[1] In the case of tetramethylethylene, of course, no α-nitroolefin can be formed; however, as would be expected from the previously proposed mechanism, this does not interfere with the formation of a β-nitroolefin. As was also the case with isobutylene, conducting the reaction in the absence of excess liquid olefin led to an increase in the yields of those products formed *via* polar reactions. Thus, the runs with olefin vapors gave greater yields of the β-nitroolefins (ionic decomposition of the

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(4) J. Schmidt, *Ber.*, **35**, 3722 (1903).

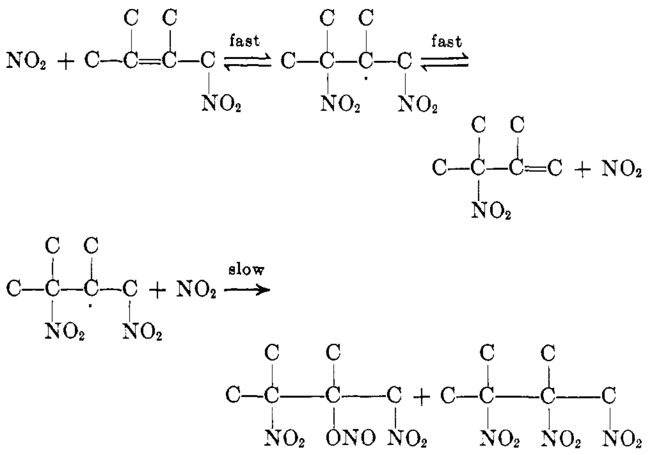
intermediate diazo nitrate) and greater yields of such substances as nitrate esters, ketones, and glycol derivatives, which are believed to be formed *via* nitrosonium ion addition processes in the primary reaction step.[2]

One respect in which the reactions of these highly branched olefins with nitric oxide differ from those of the simpler olefins is that the intermediate nitrosites appeared to be less reactive. Considerable quantities of unreacted monomeric nitrosites were present in our reaction products, dimerization of the nitrosites occurred slowly or not at all, and there seemed to be relatively little reaction between the nitrosites and the intermediate nitro alkyl radicals. The latter reaction, which would presumably give tris(nitroalkyl)hydroxylamines or tetrakis(nitroalkyl)dihydroxydrazines,[1] would lead to the formation of an α-nitroolefin (III) from trimethylethylene and nonvolatile residues from tetramethylenethylene.

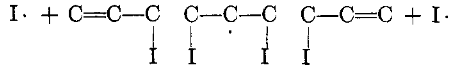
The older literature on the nitration of trimethylethylene with nitric acid[5] or "nitrous fumes,"[6] and that of *t*-amyl alcohol with nitric acid,[7] contains several reference to the formation of a "nitroisoamylene." The structure of this product has been reported as 2-methyl-3-nitro-2-butene, although its homogeneity does not seem to have been clearly established. The present finding that the "nitroisoamylene" from the nitric oxide nitration is a mixture of three closely boiling isomers suggests that the products previously obtained were also mixtures. In support of this conclusion, we may note that the "3-nitro-2-methyl-2-butene" fraction obtained by Michael and Carlson[6] gave a thiophenol adduct in only 15% yield[6] and had a refractive index between those of I and II, while pure 2-methyl-3-nitro-2-butene (III) is now known to have a much higher index. We have also observed that the nitration of trimethylethylene with absolute nitric acid likewise gives the three isomers, I, III, and III.

The Allylic Rearrangement of β-Nitroolefins.—The results showed that two isomeric β-nitroolefins were obtained from purified trimethylethylene or tetramethylethylene rather than just the one predicted by the nitration mechanism.[2] Three explanations for this finding were considered: (a) direct substitution of allylic hydrogens; (b) isomerization of the olefins, followed by normal nitric oxide–olefin reactions; and (c) isomerization of the expected β-nitroolefins I and IX. The first two explanations were readily eliminated. First, it has been observed that the allylic substitution process (*e.g.*, as in the reactions of nitric oxide, nitrogen dioxide, or dilute nitric acid with toluene or other aralkyl hydrocarbons) requires temperatures above about 120°, and gives large quantities of allylic alcohols, aldehydes, nitrates, acids, etc., in addition to nitro compounds. These were not observed in the olefin nitration products. Second, if the tetramethylethylene had first isomerized to 2,3-dimethyl-1-butene, considerable quantities of 2,3-dimethyl-1-nitro-1-butene and 3-methyl-2-(nitromethyl)-1-butene would have been expected. These could not be detected spectroscopically in our product fractions. The third explanation, namely, that the β-nitroolefins formed in the reaction are capable of undergoing allylic rearrangement, appears to be consistent with all of our observations. In particular, it is supported by the finding that nitrogen dioxide, which is known to be present in nitric oxide–olefin nitration systems, can indeed effect the interconversion of the isomeric β-nitroolefins.

We propose the following mechanism for this NO_2-catalyzed allylic rearrangement of β-nitroolefins such as the dimethylnitrobutenes.



The mechanism is thus suggested to be analogous to the allyl iodide–iodine exchange process[8] in depending upon the reversibility of the addition of a free radical to an olefin.



$$I\cdot + C{=}C{-}\underset{I}{C} \quad \underset{I}{C}{-}\dot{C}{-}\underset{I}{C} \quad \underset{I}{C}{-}C{=}C + I\cdot$$

There are three other observations which also suggest that the addition of nitrogen dioxide to an olefin to give a β-nitroalkyl radical is reversible. First, we have noted that the nitrosite of isobutylene can be partically decomposed into its components on heating.[1] The dissociation of an aliphatic nitroso compound into nitric oxide and a radical is known to occur easily,[9] and in the case of the nitrosite this would give a β-nitroalkyl radical which could then regenerate the olefin by loss of nitrogen dioxide. Second, it has been observed that the photochemical chlorination of anhydrous nitro paraffins, presumably *via* the usual free-radical chain process, is abnormally slow.[10] Evidently the kinetic chains are interrupted somehow; an attractive explanation is that this occurs through the loss of nitrogen dioxide from β-nitroalkyl radicals. Third, the reversibility of the NO_2-olefin reaction makes possible a rational interpretation of the NO_2-catalyzed *cis–trans* isomerization of olefins.

The NO_2-Catalyzed *cis–trans* Isomerization of Olefins.—The NO_2-catalyzed *cis–trans* isomerization of olefins is probably the oldest known isomerization reaction. The conversion of the liquid fat, olein, to the solid fat, elaidin, by "nitrous acid" has been known for

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(5) H. Wieland and F. Rahn, *Ber.*, **54**, 1775 (1921).

(6) A. Michael and G. H. Carlson, *J. Org. Chem.*, **4**, 169 (1939).

(7) L. Haitinger, *Monatsh.*, **2**, 286 (1881).

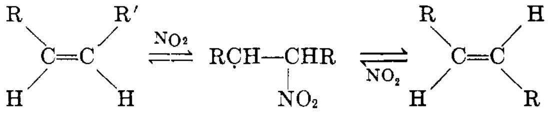
(8) D. J. Sibbett and R. M. Noyes, *J. Am. Chem. Soc.*, **75**, 763 (1953).

(9) W. Schlenk, L. Mair, and C. Bornhardt, *Ber.*, **44**, 1169 (1911).

(10) G. D. Jones, J. Zomlefer, and K. Hawkins, *J. Org. Chem.*, **9**, 500 (1944); D. C. Sayles and E. F. Degering, *J. Am. Chem. Soc.*, **71**, 3161 (1949).

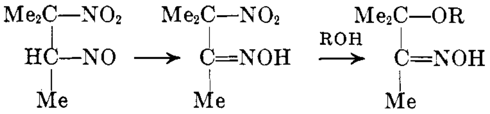
about three hundred years,[11] although the elaidin was not obtained in a pure state until 1832.[12] The reaction has also been applied to the interconversion of oleic and elaidic acids,[13,14] maleic and fumaric acids,[15] *cis*- and *trans*-stilbene,[16] erucic and brassidic acids,[14] *cis*- and *trans*-petroselenic acids,[14] and β- and γ-caryophyllene.[17]

Four facts are known about this isomerization. (a) A variety of agents capable of supplying nitrogen dioxide may be used as the catalysts, including nitric acid in which mercury[11-14] or starch[13] has been dissolved, nitrous fumes,[13] nitrogen dioxide,[13] or nitric oxide.[18] (b) The reaction is an equilibrium process and the final product is the same whether the *cis* or *trans* isomer is isomerized.[14] (c) The usual N_2O_4-olefin adducts (nitro alcohol, nitrosite) are always formed during the isomerization; in order to get predominately isomerization rather than adduct formation, it is necessary to use only small quantities of the catalyst.[14,15] (d) The N_2O_4-olefin adducts obtained are stable under the conditions of the reaction,[19] and only in special cases can they be converted back to the olefins on heating. These data, coupled with the present finding that the addition of nitrogen dioxide to an olefin to give a β-nitro alkyl radical is reversible, establish the following mechanism for the isomerization.



The Nitrosite Rearrangement.—In 1903 Schmidt found that trimethylethylene nitrosite (VI) dissolved slowly in cold alkali and, upon acidification, gave a colorless solid isomer.[20] This isomer (VIc) was found to be an oxime which gave sodium nitrite when warmed with sodium hydroxide. Later, Deussen found that the blue β-caryophyllene nitrosite could similarly be converted to a colorless, solid isomer.[21] In addition, he found that this oxime, the original nitrosite, β-caryophyllene nitrosochloride, and both isomers of γ-caryophyllene nitrosochloride all reacted with alkaline reagents with loss of nitrate or chloride to give identical derivatives (α-benzylamino oxime, α-ethoxy oxime, etc.). Similarly, we have now found that trimethylethylene nitrosite reacts with methanolic KOH to give an α-methoxyoxime identical with that obtained *via* the similar treatment[22] of trimethylethylene nitrosochloride, nitrobromide, or nitrosate. In addition, there are formed the oxime ether polymers resulting from the displacement of a nitro group on one nitrosite residue by the oxime hydroxyl of another.

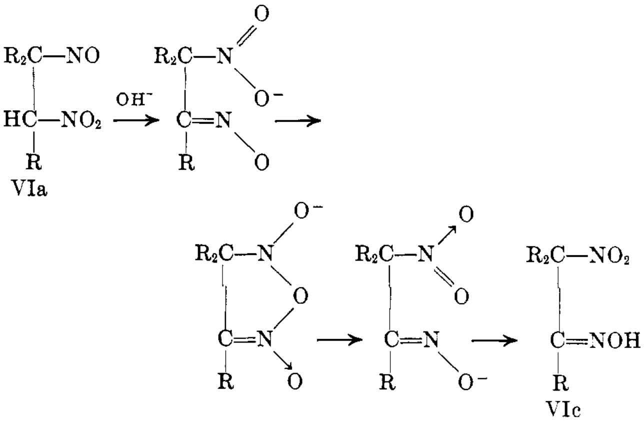
These transformations under alkaline conditions at first attracted little attention since the older workers believed that the nitrosites of the trialkylethylenes contained secondary nitroso and tertiary nitro (or nitrite) groups. Thus, the oxime formation and displacement reactions could be very simply formulated.



$$\begin{array}{c}\mathrm{Me_2C{-}NO_2}\\ |\\ \mathrm{HC{-}NO}\\ |\\ \mathrm{Me}\end{array} \longrightarrow \begin{array}{c}\mathrm{Me_2C{-}NO_2}\\ |\\ \mathrm{C{=}NOH}\\ |\\ \mathrm{Me}\end{array} \xrightarrow{\mathrm{ROH}} \begin{array}{c}\mathrm{Me_2C{-}OR}\\ |\\ \mathrm{C{=}NOH}\\ |\\ \mathrm{Me}\end{array}$$

VIb VIc

However, the observation that the trimethylethylene nitrosite actually contains secondary nitro and tertiary nitroso groups (*i.e.*, has structure IVa) indicates that a rearrangement is required in order to form VIc and the α-substituted oximes. We propose to denote this shift as the *nitrosite rearrangement*, and suggest the following mechanism for it.



VIa

VIc

The nitro oxime thus formed can, of course, react further under the alkaline conditions of the reaction to give other α-substituted oximes.

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[11] The discovery of this phenomenon has been attributed to Boyle in 1661; see A. W. Ralston, "Fatty Acids and Their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 110. Its nature appears to have been clearly defined by the end of the eighteenth century; the "American Edition of the Encyclopedia," Vol. 8, Philadelphia, Pa., 1790, p. 475, states, "Expressed oils, as well as all other fatty or unctuous substances, are considerably thickened and hardened by their union with the nitrous acid. There is only one preparation where this combination is applied to use. It is the *ungentum citrinum* of the shops. This is made by adding some quantity of melted hog's lard to a solution of quicksilver in the nitrous acid. The acid, though in a diluted state, and combined with the mercury, nevertheless acts with such force on the lard as to render the ointment almost of the consistency of tallow."

[12] F. Boudet, *Ann.*, **4**, 1 (1832).

[13] H. Meyer, *ibid.*, **35**, 174 (1840); J. Gottlieb, *ibid.*, **67**, 52 (1846).

[14] H. N. Griffith and T. P. Hilditch, *J. Chem. Soc.*, 2135 (1932).

[15] J. Schmidt, *Ber.*, **33**, 3241 (1900).

[16] C. Keller and A. Schwartz, *ibid.*, **45**, 1946 (1912).

[17] G. E. Deussen and A. Lewisohn, *Ann.*, **356**, 30 (1902); A. Aebi, D. H. R. Barton, and A. S. Lindsey, *J. Chem. Soc.*, 3124 (1953).

[18] K. Fuse and B. Tamamuski, *J. Chem. Soc. Japan*, **64**, 338 (1943).

[19] I. Egorov, *J. Russ. Phys. Chem. Soc.*, **35**, 973 (1903); *J. prakt. Chem.* **86**, 539 (1912).

[20] J. Schmidt, *Ber.*, **35**, 2323 (1903).

[21] E. Deussen and A. Lewinsohn, *Ann.* **356**, 17 (1907).

[22] J. Schmidt, *Ber.*, **35**, 3722, 3736 (1903).