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PHOTOLYSIS OF NITROSO COMPOUNDS—III

2-NITRO-2-NITROSOPROPANE

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Abstract—The photodecomposition of 2-nitro-2-nitrosopropane (2-propylpseudonitrole) with light of $\lambda > 540$ nm was studied. The product distribution changes drastically with the nature of the solvent but can be explained readily by homolytic cleavage of the C–NO bond. No evidence of photoreduction by an excited state of the nitrosocompound was obtained.

In aprotic solvents the major products were acetone, 2,2-dinitropropane, 2-nitropropene, nitrogen dioxide, nitric oxide and nitrogen. In methanol methyl nitrite, acetoxime, acetone dimethylketal and acetone together with dinitrogen monoxide and water were the main products. This pronounced solvent influence is shown to be caused by the solvolysis (in methanol) or secondary thermal decomposition (in aprotic solvents) of labile intermediates.

The 2-nitropropyl radical formed in the primary dissociative step does not take part in any hydrogen abstraction reactions under the experimental conditions employed.

INTRODUCTION

A number of studies of the photolysis of *gem*-substituted aliphatic nitroso compounds (RR'CXNO) have recently been published.[1-3] Our own studies were undertaken to study how the photochemistry of these compounds is influenced by the nature of X, in particular when X varies from alkyl to Cl, Br, NO_2, OAc and CN. Our studies* indicate[4-6] that homolytic cleavage of the C–NO bond of the excited nitroso compound invariably appears to be the dominating dissociative mode independent of the substituent X or the nature of the solvent. The varying product distributions are due to extensive secondary dark reactions. The stability and reactions of the nitroxides formed by scavenging of the photolytically generated radicals RR'CX and NO is of prime importance in rationalizing experimentally observed stable products.

In the present communication we report a re-examination of the red-light photolysis of 2-nitro-2-nitrosopropane, previously studied by Hammick.[7] He interpreted his results in terms of two primary steps, namely photoxidation and elimination of HNO. The quantum yields and kinetics of the photodecomposition are known from this study, but the lack of information concerning the photolysis products cast some doubts on the validity of this interpretation and necessitated a re-investigation.

RESULTS

Table 1 summarizes the analytical results obtained by red-light photolysis of 2-propylpseudonitrole in methanol. The main products are methyl nitrite, acetoxime, acetone dimethyl ketal and acetone. The presence of water and in some samples also of dinitrogen monoxide is noteworthy. The yield of the latter is apparently very high if solutions with high initial concentrations of nitroso compounds are photolyzed (Experimental) and causes the unsatisfactory balance of nitrogen. Analytical results depended on whether or not the solutions were analysed quickly after completed photolysis, suggesting the influence of dark reactions. Formaldehyde, 2-nitropropane, 2-nitropropene and 2,2-dinitropropane were absent in alcoholic solvents.

A change of the solvent from methanol to isopropanol results in the formation of isopropyl nitrite instead of methyl nitrite. Nitrite yields in both solvents generally corresponded to almost 1 mole per mole nitroso compound, but these yields decrease markedly however in dilute solutions (10^{-3} molar) in the presence of oxygen. The effect of oxygen on nitrite yields is less pronounced at initial concentrations bigger than 5×10^{-2} M and virtually negligible at an initial concentration of pseudonitrole of 0·1 M under the specific conditions employed (high light intensity, room temperature and static system without attempts to keep the solution saturated with oxygen).

In order to prove that the product distribution obtained by photolysis in alcohols is predominantly

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*Publication of our results with *gem.* halogen and cyanonitroso compounds is in progress.

Table 1. Products of the photolysis of 2-nitro-2-nitrosopropane in methanol

Initial concentration (10^{-2} M)	Yields in m mole/100 m mole of nitroso compound A	B	C	D	E	F
1·4	102	4·3	29	51	+[a]	−[a]
5·6	103	8·3	36	49	+	−
13·8	106	20·0	22	46	+	+
13·8[c]	87	53·0	16	29	+	+
0·33	106					
0·29[b]	57					

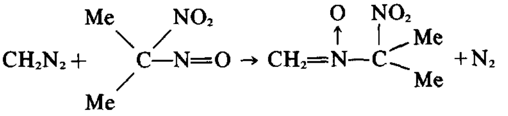
A = methyl nitrite, B = acetone, C = 2,2-dimethoxypropane, D = acetoneoxime, E = water, F = dinitrogen monoxide.

[a] + = present but not quantitatively determined, − = not found.

[b] In presence of oxygen.

[c] Previous solution analysed 15 min. after completed photolysis

governed by the solvolysis of an intermediate α-nitronitrone or its protonated form we prepared the analogous compound methylene-N-2-nitro-2-propylnitrone by the action of diazomethane upon 2,2-nitronitrosopropane monomer *in situ* and analysed the products. Acetoxime, methyl nitrite and formaldehyde dimethyl acetal, along with hydrolysis products were the main reaction products.



$$\mathrm{CH_2N_2 + Me_2C(NO_2){-}N{=}O \rightarrow CH_2{=}\overset{\overset{O}{\uparrow}}{N}{-}C(NO_2)Me_2 + N_2} \qquad (1)$$

Attempts to trap the dimethyl analogue postulated as an intermediate in the photolysis by 1,3-dipolar addition to ethyl acrylate were unsuccessful.

In contrast to the alcohol solvents, photolysis in the aprotic solvents benzene, chloroform, 1,4-diisopropylbenzene and diethylether afforded nitrogen dioxide, nitrogen and nitric oxide as well as small amounts of dinitrogen monoxide. As seen from the analysis results collected in Table 2 the major organic products were acetone, 2,2-dinitropropane and varying amounts of 2-nitropropene. The relative yields of these products varies depending upon the particular solvent used. Within the experimental conditions employed, neither the presence of air (static system—stoppered vessels) nor the use of white light from tungsten filament lamps instead of orange-red light had any significant influence upon the product distribution. It must be emphasised, however, that the purity of solvents particularly with regard to hydroxylic contaminants (water, alcohols and hydroperoxides) is essential for experiments in dilute solutions. Formation of nitrogen dioxide was absent in impure solvents, whereas acetoxime was observed as an additional product if unpurified solvents were used. Traces of 2-nitropropane could only be detected if unrecrystallised starting material was used.

Photolyses in aprotic solvents in the presence of added nitrogen dioxide increased the yield of 2,2-dinitropropane while decreasing that of acetone and 2-nitropropene without however fundamentally changing the product distribution. On the other hand, if the accumulation of oxides of nitrogen (nitric oxide and nitrogen dioxide) formed during the photolysis was prevented by addition of excess 2-methyl-2-butene then 2-nitropropene disappeared almost completely and a considerable decrease of both acetone and 2,2-dinitropropane also resulted. The overall balance of these products decreases from virtually 100% in the absence of added alkene to less than 40% in its presence.

The kinetic investigation of the thermal decomposition and the direct oxidation of 2-nitro-2-nitrosopropane monomer by nitrogen dioxide/tetroxide in chloroform revealed both reactions to be too slow to influence product distributions obtained by photolysis. Plots of log absorbancy of the nitroso compound versus time gave reasonably straight lines indicating the reaction to be near to first order in nitroso compound. Calculated first order rate constants varied from $3{\cdot}7 \times 10^{-4}\ \mathrm{min}^{-1}$ in the absence of NO_2 to $5{\cdot}5 \times 10^{-4}\ \mathrm{min}^{-1}$ in the presence of a 1·8 fold excess of nitrogen dioxide in solutions $3{\cdot}2 \times 10^{-2}$ M in nitroso compound at 12°. Products of the thermal decomposition in chloroform included acetone, 2,2-dinitro-

Table 2. Products of the photolysis of 2-nitro-2-nitrosopropane in aprotic solvents

Solvent	Initial concentration (10^{-2} M)	Yields in m mole/100 m mole nitroso compound A	B	C	D
C_6H_6*	15·7	49	30	2·0	+[a]
C_6H_6	1·40	58	26	2·9	+
$CHCl_3$	2·62	71	18	8·8	+
$CHCl_3$[b]	2·62	64	29	5	
$CHCl_3$[c]	2·62	61	39	<1	
$CHCl_3$[d]	4·0	29	9·7	<0·1	−
Et_2O	13·6	41	47	9·7	+
1,4-diisopropylbenzene	5·2	66	24	9·5	+

A = Acetone, B = 2,2-dinitropropane, C = 2-nitropropene, D = nitrogen dioxide/tetroxide.

[a] Present, but not quantitatively analysed (+) or absent (−) respectively.

[b] In presence of an equivalent amount of nitrogen dioxide.

[c] In presence of a tenfold excess of nitrogen dioxide.

[d] In presence of excess 2-methyl-2-butene.

*Gaseous products of this experiment in m mole/100 m mole nitroso compounds: nitrogen (37), nitric oxide (8·4), nitrogen dioxide (1), traces of dinitrogen monoxide and carbon dioxide.

propane, traces of 2-nitropropene, nitrogen dioxide and unknowns. The product balance is unsatisfactory and the distribution of products (Experimental) is distinctly different from that obtained by photolysis.

2-Nitro-2-nitrosopropane solutions in chloroform have been found to absorb nitric oxide with formation of a labile intermediate which after rearrangement decomposes with evolution of nitrogen (compare Bamberger's reaction[8,9]). The reaction is slower and less efficient than the related reaction of *gem*-chloronitroso compounds in alcohols* explaining why the pseudonitrole has been claimed not to undergo the Bamberger reaction.[10] The product distribution obtained in this dark reaction is summarised together with the other data in Table 3.

DISCUSSION

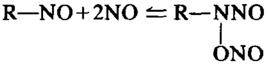
Hammick[7] has shown that the photolysis of some *gem*-substituted nitroso compounds is twice as efficient in alcoholic solvents as in aprotic solvents. It is known[1-3] that the product distribution in the photolysis of *gem.*-chloronitroso compounds depends markedly upon the solvent with nitrite formation[5,6] in alcoholic solvents. Oxime formation in the photolysis of alcoholic solutions of *gem.*-substituted nitroso compounds is due to solvolysis and not to photoreduction[2 11] or to hydrogen abstraction by an iminoxy radical.[11] We propose that the formation of nitroxides is general to the photolysis of C-nitroso compounds (*cf* thermolysis[12-14] and one direct study of photolysis[15]). Nitrites are then formed as a result of the combination of the nitroxides with nitric oxide[16 17] followed by solvolysis.[18] Scheme 1 (Eqs 2–12) summarises our major mechanistic conclusions, reactions (8)–(12) being necessary to account both for the observed nitrite yield per mole of nitroso compound decomposed and for the production of acetoxime and acetone dimethyl ketal.

Scheme 1(R = Me_2CNO_2)

$$R{-}NO \xrightarrow{h\nu} R{-}NO^* \longrightarrow R^\cdot + {}^\cdot NO \qquad (2)$$

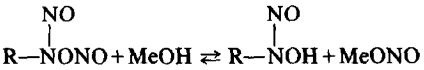
$$R^\cdot + R{-}NO \longrightarrow \underset{1}{R_2NO^\cdot} \qquad (3)$$

$$R_2NO + NO \rightleftarrows \underset{2}{R_2NONO} \qquad (4)$$

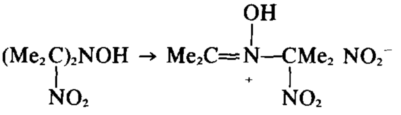


$$R{-}NO + 2NO \leftrightharpoons \underset{\substack{ONO\\3}}{R{-}NNO} \qquad (5)$$

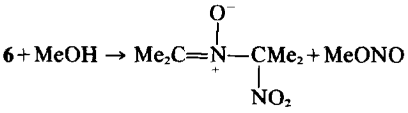
$$R_2NONO + MeOH \rightleftarrows \underset{4}{R_2NOH} + MeONO \qquad (6)$$



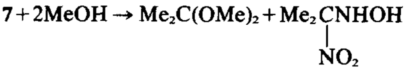
$$\overset{NO}{R{-}NONO} + MeOH \rightleftarrows \underset{5}{\overset{NO}{R{-}NOH}} + MeONO \qquad (7)$$



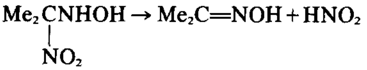
$$\underset{\substack{NO_2\\4}}{(Me_2C)_2NOH} \rightarrow Me_2C{=}\overset{OH}{\overset{+}{N}}{-}\underset{\substack{NO_2\\6}}{CMe_2}\ NO_2^- \qquad (8)$$



$$6 + MeOH \rightarrow Me_2C{=}\overset{O^-}{\overset{+}{N}}{-}\underset{\substack{NO_2\\7}}{CMe_2} + MeONO \qquad (9)$$



$$7 + 2MeOH \rightarrow Me_2C(OMe)_2 + Me_2\underset{NO_2}{C}NHOH \qquad (10)$$

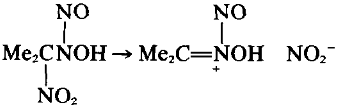


$$Me_2\underset{NO_2}{C}NHOH \rightarrow Me_2C{=}NOH + HNO_2 \qquad (11)$$

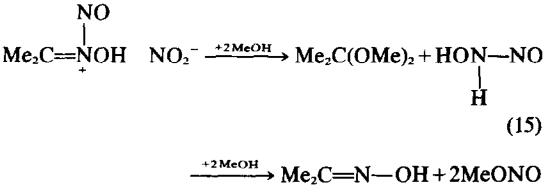
$$HNO_2 + MeOH \rightleftarrows MeONO + H_2O \qquad (12)$$

Nitrous oxide formation is due to reaction (13)[19] and possibly to solvolysis of **5** via (14)–(16).

$$Me_2C{=}NOH + HNO_2 \rightarrow Me_2C{=}O + N_2O + H_2O \qquad (13)$$

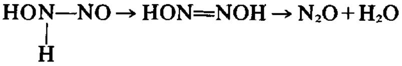


$$Me_2\underset{NO_2}{C}\overset{NO}{N}OH \rightarrow Me_2C{=}\overset{NO}{\underset{+}{N}}OH\ \ NO_2^- \qquad (14)$$



$$Me_2C{=}\overset{NO}{\underset{+}{N}}OH\ \ NO_2^- \xrightarrow{+2MeOH} Me_2C(OMe)_2 + HO\underset{H}{N}{-}NO \qquad (15)$$

$$\xrightarrow{+2MeOH} Me_2C{=}N{-}OH + 2MeONO$$

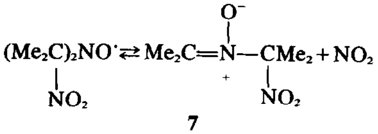


$$HO\underset{H}{N}{-}NO \rightarrow HON{=}NOH \rightarrow N_2O + H_2O \qquad (16)$$

$$Me_2C(OMe)_2 + H_2O \rightarrow Me_2CO + 2MeOH \qquad (17)$$

Reactions (13)–(17) should be important in concentrated solutions, where our results show very low oxime and ketal yields and markedly increased yields of nitrous oxide and acetone.

Direct β-cleavage of the nitroxide with formation of nitrone **7** and nitrogen dioxide[20] (18) is an alternative to (4).



$$\underset{NO_2}{(Me_2C)_2NO^\cdot} \rightleftarrows Me_2C{=}\overset{O^-}{\overset{+}{N}}{-}\underset{\substack{NO_2\\7}}{CMe_2} + NO_2 \qquad (18)$$

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*Formation of alcohol nitrite, oximes and ketones has been demonstrated in this case.[6]

Table 3. Products of the thermal decomposition[a] (2) and of the dark reaction of 2-nitro-2-nitrosopropane with nitric oxide[b] (1) in chloroform

	Yields in m mole/100 m mole nitroso compound			
	Acetone	2,2-Dinitropropane	2-Nitropropene	Nitrogen dioxide
1	23·3	12·6	29·2	+[c]
2	37	34	<0·1	+

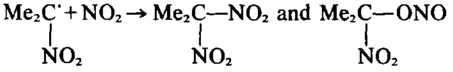
[a]Five days at room temperature, initial concentration 0·352 M.

[b]Yields corrected for 5% of unchanged starting material, for details see Experimental part.

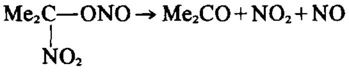
[c]Present but not quantitatively analysed.

Although attempts to scavenge intermediary **7** by 1,3-dipolar cycloaddition using ethyl acrylate as dipolarphile were unsuccessful, the *in situ* formation and subsequent methanolysis of a related nitrone, methylene-N-2-nitropropyl nitrone (1), gave results consistent with the proposed solvolysis scheme for **7**.

For aprotic solutions Scheme 1 and reaction (18) will still occur. The accumulation of nitric oxide and nitrogen dioxide in the absence of hydroxylic solvents causes the main change in the product pattern. Photolytically generated 2-nitropropyl radicals will be scavenged by nitrogen dioxide, resulting in formation of the stable *gem.* dinitro compound and the labile *gem.* nitronitrite (19), which decomposes into acetone[21] via reaction (20).



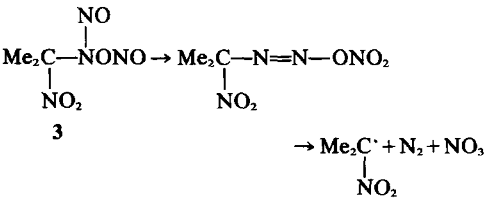
$$\text{Me}_2\underset{\text{NO}_2}{\text{C}^{\cdot}} + \text{NO}_2 \rightarrow \text{Me}_2\underset{\text{NO}_2}{\text{C}}\text{—NO}_2 \text{ and } \text{Me}_2\underset{\text{NO}_2}{\text{C}}\text{—ONO} \quad (19)$$



$$\text{Me}_2\underset{\text{NO}_2}{\text{C}}\text{—ONO} \rightarrow \text{Me}_2\text{CO} + \text{NO}_2 + \text{NO} \quad (20)$$

Acetone may also be formed from reaction of nitrogen dioxide with nitrone **7**.

The accumulation of nitric oxide will result in an increased formation of the starting material (reverse of 2). Nitrogen is formed via sequence (21).



$$\text{Me}_2\underset{\text{NO}_2}{\text{C}}\text{—}\overset{\text{NO}}{\text{N}}\text{ONO} \rightarrow \text{Me}_2\underset{\text{NO}_2}{\text{C}}\text{—N=N—ONO}_2 \rightarrow \text{Me}_2\underset{\text{NO}_2}{\text{C}^{\cdot}} + \text{N}_2 + \text{NO}_3 \quad (21)$$

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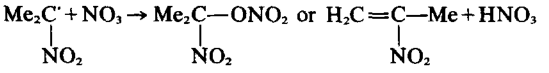
The 2-nitropropyl/NO$_3$-radical pair may recombine or disproportionate (22).



$$\text{Me}_2\underset{\text{NO}_2}{\text{C}^{\cdot}} + \text{NO}_3 \rightarrow \text{Me}_2\underset{\text{NO}_2}{\text{C}}\text{—ONO}_2 \text{ or } \text{H}_2\text{C}{=}\underset{\text{NO}_2}{\text{C}}\text{—Me} + \text{HNO}_3 \quad (22)$$

Whereas 2-nitropropene is a stable observed product the gem. nitronitrate is unstable and decomposes into the carbonyl compound and nitrogen dioxide.[20] The major role played by nitrogen dioxide in the aprotic system is substantiated by the fact that even a tenfold molar excess does not alter the product distribution fundamentally whereas excess 2-methyl-2-butene does so markedly by preventing the accumulation of nitrogen dioxide.

The absence of 2-nitropropane and acetoxime in all aprotic solvents indicates that hydrogen abstraction by the 2-nitropropyl radical or an excited state of the nitroso compound are not important in this system.

EXPERIMENTAL

Instruments and apparatus. Gas chromatographic analyses were performed on a dual column F. & M. Model 720 instrument equipped with thermal conductivity cells and a Honeywell strip chart recorder using Helium as carrier gas. UV and visible spectra were obtained from a Beckmann DK-2 spectrophotometer which was also used for quantitative analyses. IR spectra were run on a Perkin-Elmer 457 grating instrument.

Preparative scale white light irradiations were carried out employing a magnetically stirred cylindrical vessel of 100 ml volume equipped with a cooling jacket fed with tap water. Four 100 watt tungsten filament lamps surrounding the irradiation vessel served as light sources.

Irradiations with orange-red light were accomplished by exposing the solutions in Schlenk tubes to the light of a tubular 400 W high pressure sodium lamp (Osram Na-VT-400) operated with the power supply recommended by the manufacturer. The lamp was fitted into a water-cooled immersion well and was situated in the centre of a large 61-silvered Dewar filled with concentrated aqueous potassium bichromate solution which served as a cut-off filter for light of wavelengths below 540 nm. The Schlenk tubes containing the solns were suspended on the inside wall of the Dewar. The resulting arrangement was found to minimise exposure times by the use of high light intensity thereby facilitating the avoidance of secondary dark reactions of photoproducts. Exposure times varied from 5 to 30 min depending on the concentration of the starting material, solvent and the presence of oxygen. Unless otherwise stated all irradiations were carried out with vacuum degassed solutions (vacuum: 10^{-4} mm Hg) under an oxygen and moisture free atmosphere of nitrogen. Photolyses in the presence of air were carried out in ordinary stoppered measuring flasks.

Solvents. MeOH was refluxed over Mg turnings, EtOH free chloroform, thiophene free benzene and 1,4-diisopropylbenzene were passed over columns of freshly activated alumina (Woelm W200 basic, Act. Super 1) under N_2. Diethyl ether was refluxed over Na wire, stored over LAH and re-condensed in vacuum prior to use. All the solvents were distilled and stored under N_2.

Starting material and reference compounds. 2-Nitro-2-nitrosopropane was obtained in excellent yield by nitrosation of 2-propanenitronic acid similar to the procedure developed by Noland and Libers[22] for other pseudonitroles. The method is superior to the published preparations[7 23-26] and was applied as follows:

2-Nitropropane (45 g; 0·5 mole) were dissolved in a soln of KOH (42 g; 0·75 mole) in 150 ml water employing a stoppered flask and shaking the mixture with external cooling with tap water until the nitropropane layer had disappeared. After addition of 38 g (0·55 mole) sodium nitrite the resulting soln was pre-cooled to −10° and then added all at once to a vigorously stirred soln of 50 ml conc H_2SO_4 in 300 ml iced water, cooling externally with an ice–salt mixture. Stirring was continued in the dark for 30 min during which time the monomer had dimerized. Suction filtration followed by rinsing of the crude white product and drying yielded 51·6 g (92%). Two recrystallizations from ether afforded 40·5 g (72%) of crystalline, white pseudonitrole of m.p. 75·5° (dec), Lit: 76°.[25]

2-Nitropropane, 2,2-dimethoxypropane, acetone and 2-methylbutene were commerical products and purified by fractional column distillation, acetoxime was purified by resublimation

2-Nitropropane and 2,2-dinitropropane were obtained according to (27) and (28) respectively. Nitrogen dioxide was purified by distillation in a stream of dry oxygen over P_2O_5 and cylinder nitric oxide (BASF) by passing the gas over beds of KOH and P_2O_5.

Photolysis of concentrated solutions of 2-nitro-2-nitrosopropane and analysis of gaseous products

(a) *Irradiation of methanolic solns with white light.* Mixtures of 7 to 10 g of the pseudonitrole and 100 ml methanol containing undissolved crystalline dimer evolved large amounts of a condensable gas after an induction period of 5 min. The gas was condensed in a trap cooled with dry ice/acetone. The faintly yellowish liquid was brought to a temp of −14° by means of an ice/salt mixture after photolysis was complete (4 to 6 h), whereupon a colourless gas evolved which was identified as dinitrogen monoxide by gas IR spectroscopy (absorption at 2230 cm^{-1}) and gas adsorption chromatography employing a 6′ stainless steel ¼″ Porapak a (60/80 mesh) column. The yellowish liquid that had remained in the trap boiled below 0°, absorbed strongly in the IR at 1625 and 1675 as well as 990 and 810 cm^{-1} and therefore suggested methylnitrite. Examination of the UV spectrum of a methanolic soln confirmed this conclusion by observation of the characteristic banded spectrum of a nitrite with the highest maximum at 352 nm. Vapour phase chromatography (12′, ¼″, 4% tetraethyleneglycol dimethylether on 60/80 Chr.G at room temp) followed by IR spectroscopic examination of the eluted component together with comparison of retention times with an authentic sample of methylnitrite confirmed this assignment.

The clear and almost colourless MeOH soln still contained large amounts of methyl nitrite. The products acetone and 2,2-dimethoxypropane were analyzed as described separately: 88% acetone, 7% 2,2-dimethoxypropane.

Acetoxime was present only in traces. Removal of the solvent on a rotary evaporator afforded an involatile residue corresponding to less than 2% by weight. In the distillate acetone was precipitated and characterised as its DNP-hydrazone.

(b) *Irradiation of benzene solutions with orange-red light.* In a typical experiment 1·80 g (15·2 moles) nitroso compound in 100 ml benzene were irradiated under H_2. After an 8 min induction period gas evolution started. The brownish gas was collected in a silicon oil gas burette. Photolysis is finished after 30 min and resulted in the evolution of a total of 160 ml gas (reduced to standard conditions). The gas evolution continued for another 30 min. Samples (0·25 ml) were withdrawn with a gas injection syringe and analysed by gas adsorption chromatography. Nitrogen and nitric oxide were determined by means of a ¼″, 6′, molecular sieve 5 Å (60/80 mesh) column, carbon dioxide and dinitrogen monoxide by means of a similar Porapak Q-column. (Table 2). All gaseous components except nitrogen were additionally identified by IR spectroscopy. For nitric oxide the finely structured double band with zero centre was observed at 1869 cm^{-1}, the one at 1621 cm^{-1} was assigned to nitrogen dioxide. The band observed at 1800 cm^{-1} was due to nitrosyl chloride formed by reaction of nitrogen dioxide with the sodium chloride windows of the gas cell. Products in soln were analysed as soon as the gas evolution stopped after removing dissolved nitrogen dioxide with a little concentrated aqueous bicarbonate soln and drying of the organic layer.

Photolysis of dilute solutions in various solvents. Samples were prepared by weighing the crystalline dimer into 50 ml measuring flasks previously filled with N_2. After dissolution in the appropriate solvent samples were either transferred under N_2 into Schlenk tubes and subsequently degassed on a standard vacuum line or else directly photolysed in the stoppered flasks under N_2. Methanolic* solns were colourless after completed photolysis whereas the aprotic solutions were yellow to brown coloured by the formation of nitrogen dioxide, which was removed immediately after completed photolysis. If this was not removed and samples were left standing for some time the yields of acetone and 2-nitropropene decreased rapidly. 2-Nitropropane and acetoxime were absent in all aprotic solvents 2-Nitropropane, 2-nitropropene and 2,2-dinitropropane as well as formaldehyde were absent in methanolic solutions.

Dark reaction of 2-nitro-2-nitrosopropane with nitric oxide. A 15 ml portion of a $5{\cdot}1\times10^{-2}$ M soln of the pseudonitrole in chloroform was vacuum degassed in a 250 ml Schlenk tube. Nitric oxide was admitted at room temp up to a total pressure of approximately 950 mm mercury. The magnetically stirred soln turned green by formation of nitrogen dioxide with simultaneous evolution of N_2 after an induction period of 5 min. After further 20 min of stirring at room temp the green brown soln was frozen with liquid N_2 and permanent gases pumped off. Upon rewarming nitrogen dioxide evaporated partly into the dead space over the soln. After admission of air and removal from the vacuum line the soln was stirred with 1 ml of sat aqueous bicarbonate soln until all nitrogen dioxide was removed. The slightly bluish organic layer was dried and

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*For complete dissolution of the pseudonitrole methylene chloride was employed as cosolvent.

analysed for unreacted pseudonitrole by visible spectrometry. The analytical results are collected in Table 3.

Thermal decomposition of 2-*nitro*-2-*nitrosopropane*. A soln (100 ml; 0·352 M) of the nitroso compound in chloroform as left standing over N_2 in a round bottomed flask closed to air by a mercury valve. After 5 days at room temp in the dark the nitroso compound had decomposed with formation of a yellowish, turbid soln that contained droplets of water and reacted strongly acidic. Extraction of the organic layer with bicarbonate soln afforded an orange red aqueous extract from which after acidification with HCl 0·7 g of an acidic yellow and water soluble oil of unknown composition was obtained. The chloroform layer from the first extraction afforded 1·45 g (30%) crude 2,2-dinitropropane. For analytical results see Table 3.

Kinetics of the oxidation of 2-*nitro*-2-*nitrosopropane by nitrogen dioxide*. The required volumes of a 3m stock soln of dinitrogen tetroxide in CCl_4 were added to a stirred chloroform soln of the nitroso compound. Temp constancy during a run was obtained by circulating water through a cooling jacket surrounding the reaction vessel. Access of light was prevented by painting the vessel black. The concentration of the nitroso compound was monitored at 20 min intervals of time by withdrawing samples under N_2 and quenching the reaction by removal of nitrogen dioxide with ice cold aqueous bicarbonate solution and determination of the residual absorption of the nitroso compound at $\lambda_{max} = 637$ nm.

Reaction of diazomethane with 2-*nitro*-2-*nitrosopropane*. The powdered nitroso dimer (1·18 g; 10 mmoles) was stirred in a mixture of 50 ml diethyl ether and 20 ml MeOH at 0°C. Small portions of an ethereal diazomethane soln were added waiting before each further addition until the blue colour of the monomeric nitroso compound reappeared Altogether 30 m mole of diazomethane had to be added until all dimer as well as monomer had disappeared. The reaction proceeded with formation of a colourless gas. GLC analysis (acetone, 2,2-dimethoxypropane and formaldehyde dimethylacetal) and spectrophotometry (methyl nitrite, acetoxime after conversion to 2,2-chloronitrosopropane) gave the following result· Acetone (60%), 2,2-dimethoxypropane (3·2%), methylal (2%), methyl nitrite (13%), acetoxime (17%).

Analysis and identification of products. 2,2-Dinitropropane, 2-nitropropene and acetoxime were trapped from the exit port of the gas chromatograph after chromatographic separation of concentrated solns and identified by comparison of retention times and IR spectra. Acetone and 2,2-dimethoxypropane were similarly identified. Their IR spectra were obtained by sweeping the respective GC fraction into a 10 cm IR gas cell. Methyl nitrite was identified as previously described.

Quantitative analysis of acetoxime was accomplished by conversion to 2,2-chloronitrosopropane with gaseous chlorine. Prior removal of the bulk of MeOH and dilution with chloroform followed by conversion to the chloronitroso compound gave stable solns. GLC analyses employing a 6′, ¼″ dinonylphthalate column gave identical results.

Methyl nitrite was determined by UV spectrometry. The extinction coefficient for the maximum of the strongest band at $\lambda = 352$ mμ was determined as $\epsilon_{max} = 75$ by dissolving a known amount of refractionated isopropyl nitrite in MeOH in the presence of a catalytic amount of HCl to ensure complete transesterification.

Acetone and its dimethyl ketal were determined employing two 6′, ¼″ stainless steel columns, both operated at 38° and a flow rate of 40 ml He/min. Column A (4% Carbowax 1500 on 60/80 Chr. G, AW-DMCS) gave the sum of acetone and its ketal, column B (4% tetraethyleneglycol dimethyl ether on 60/80 Chr. G, AW-DMCS) allowed direct determination of acetone, whereas the ketal was eluted with solvent. In aprotic solns acetone was determined employing a 6′, ¼″ stainless steel column (3% SE 30 on Chr. W-AW, DMCS, 60/80 mesh) with n-hexane as internal standard. In the presence of 2-methyl-2-butene in chloroform a 6′, ¼″ Carbowax 20 M column (10% on Chr. P, 60/80 mesh) had to be employed with methyl-ethylketone as internal standard. 2-nitropropene and 2,2-dinitropropane were determined with the same column and bromobenzene as internal standard.

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