THE DECOMPOSITION OF 5-SUBSTITUTED

3-NITROSO-2-OXAZOLIDONES

DISSERTATION

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INTRODUCTION

The alkaline decomposition of N-nitrosourethanes leads to very useful products. In 1894, diazomethane was prepared by the alkaline decomposition of N-nitroso-N-methylurethane.¹ Since then, many other aliphatic diazo compounds have been prepared from aliphatic N-nitrosourethanes by alkaline treatment. Cyclic N-nitrosourethanes yield acetylenes, carbonyl compounds, and cyclic carbonates upon alkaline treatment.

In 1905, 3-nitroso-2-oxazolidone, I,² upon alkaline treatment, was found to yield acetylene.

In contrast, alkaline treatment of 3-nitroso-1-oxa-3-azaspiro 4.5 decan-2-one, II, yielded 88% of hexahydrobenzaldehyde.³

1. H. von Pechmann, Ber., 27, 1888 (1894).

2. Oxazolidine is the accepted term for the ring structure shown here, and is numbered as indicated:

A. M. Patterson and L. T. Capell, "Ring Index," Reinhold Publishing Co., New York, N. Y., 1940, p. 41. In the earlier literature the term tetrahydrooxazole is used for 2-oxazolidone.

3. M. S. Newman, J. Am. Chem. Soc. 71, 378 (1949).

More detailed studies ^{1,2} of the alkaline hydrolysis of 4- and 5-substituted 3-nitroso-2-oxazolidones have been reported and are described in the next section. In addition, a brief study of the thermal decomposition of 4- and 5-substituted 3-nitroso-2-oxazolidones was made.² No other investigations of the thermal decomposition of 3-nitroso-2-oxazolidones were found in the literature.

The interesting results obtained by Newman and Edwards warranted further study of the thermal decomposition of 3-nitroso-2-oxazolidones. Accordingly, the thermal decomposition of a series of 5-substituted 3-nitroso-2-oxazolidones was investigated. The program of research involved the qualitative and quantitative determination of the products obtained when the nitroso compounds were thermally decomposed. The effect of solvents and temperature on the products of the thermal decomposition was also studied. Mixtures of compounds were obtained, and techniques for their separation and identification were worked out. The alkaline decomposition of a new compound, 3-Nitrospiro [fluorene-9',5-oxazolidin]-2-one was investigated.

-
1. M. S. Newman and A. Kutner, J. Am. Chem. Soc. 73, 4199 (1951).
 2. M. S. Newman and W. M. Edwards, J. Am. Chem. Soc. 76, 1840 (1954).

BACKGROUND

It has been shown¹ that the alkaline treatment of 5-substituted 3-nitroso-2-oxazolidones yielded aldehydes, acetylenes, ketones, and vinyl ethers as products. Some of these results are shown in Table I:

Table I
Alkaline Decomposition of 3-nitroso-2-oxazolidones¹

R ₁	R ₂	Products	Yield
---(CH ₂) ₅ ---			88%
C ₂ H ₅	C ₂ H ₅	(C ₂ H ₅) ₂ CHCHO	79%
		(C ₂ H ₅) ₂ C=CHOC ₂ H ₅ ²	74%
∅	CH ₃	∅COCCH ₃	74%
		∅CH ₂ COCH ₃	15%
∅	∅	∅COC∅	100%

On the other hand, alkaline treatment of 4-substituted 3-nitroso-2-oxazolidones yielded aldehydes, ketones, substituted allyl alcohols

1. M. S. Newman and A. Kutner, J. Am. Chem. Soc. 73, 4199 (1951).

2. Reaction run under anhydrous conditions in ethanol.

and cyclic carbonates as products. Some of these results are shown in Table II:

Table II

Alkaline Decomposition of 3-nitroso-2-oxazolidones¹

R_3	R_4	Products	Yield
---(CH ₂) ₅ ---			52%
		45%
ϕ	CH ₃	$\phi\text{CH}(\text{CH}_3)\text{-CHO}$	59%
ϕ	ϕ	$\phi_2\text{CHCHO}$ $\phi_2\text{COHCH}_2\text{OH}$	51%
ϕ	ϕ	$\phi_2\text{CHCHO}$	12%
ϕ	ϕ	$\phi_2\text{COHCH}_2\text{OH}$	22%

1. M. S. Newman and W. M. Edwards, J. Am. Chem. Soc. 76, 1840 (1954).

The thermal decomposition of 4- and 5-substituted 3-nitroso-2-oxazolidones yielded aldehydes, acetylenes, ketones, and the parent oxazolidones as products. These results are shown in Table III:

Table III

Thermal Decomposition of 3-nitroso-2-oxazolidones¹

R ₁	R ₂	R ₃	R ₄	Products	Yield
CH ₃	∅	H	H	parent oxazolidone CH ₃ C≡C∅	70%) ₂ 26%)
∅	∅	H	H	parent oxazolidone ∅COCH ₂ ∅ ∅ ₂ CHCHO	22%) 10%) ₂ 56%)
H	H	∅	∅	parent oxazolidone	87%
H	H	CH ₃	CH ₃	parent oxazolidone	4%

1. M. S. Newman and W. M. Edwards, J. Am. Chem. Soc. 76, 1840, (1954).

2. These results could not be reproduced in part, c.f. Table IV.

There is no other work pertaining to the thermal decomposition of 3-nitroso-2-oxazolidones; although, there are some studies of the thermal decomposition of N-nitrosoamides and N-nitrosolactams.

Related Work

The amino group of aromatic amines can be replaced by aryl groups with the formation of unsymmetrical diaryls by two general procedures: (1) by reaction of an aryldiazohydroxide or acetate with aromatic compounds, and (2) by reaction of the arylnitrosoacetamide with aromatic compounds.^{1,2} The first method^{3,4} involves the following two steps, illustrated by the preparation of 4-bromodiphenyl.

The second method^{5,6} involves two steps, illustrated by the preparation of 3-nitrodiphenyl:

The yields of diphenyls by these two methods are usually less than 50%.

Much evidence has been accumulated that the reactions involving both the aryldiazohydroxide and the arylnitrosoacetamide take place through a free radical mechanism,⁷ illustrated by the preparation of

1. E. Bamberger, Ber. 28, 403 (1895).

2. O. Kuhling, Ber. 28, 41, 523 (1895).

3. M. Gomberg and W. E. Bachmann, J. Am. Chem. Soc. 46, 2339 (1924).

4. M. Gomberg and J. C. Pernert, J. Am. Chem. Soc. 48, 1372 (1926).

5. W. S. M Grieve and D. H. Hey, J. Chem. Soc. 1798 (1934).

6. H. France, I. M. Heilbron, and D. H. Hey, J. Chem. Soc. 369 (1940).

7. D. H. Hey, Ann. Repts., 37, 278 (1940).

3-nitrodiphenyl:

In recent work,¹ the isomer distribution of the unsymmetrically substituted products was determined. The diphenyls were prepared by four routes:

The peroxide method gave the best yields of diphenyls. Some of the results of this investigation are as follows:

X=	relative % yield of isomers		
	o-	m-	p-
F	54.1	30.7	15.2
Cl	62.2	24.0	13.8
Br	49.3	33.3	17.4
I	51.7	31.6	16.7
ϕ	48.5	23.0	28.5

In a study of the thermal decomposition of N-nitrosolactams, the effect of ring size on the decomposition was investigated.² The mechanism proposed follows.

1. D. H. Hey et al, J. Chem. Soc. 2892 (1951); *ibid.*, 2095 (1952); *ibid.*, 44, 3412 (1953); *ibid.*, 794, 2747 (1954).

2. R. Huisgen and J. Reinertshofer, *Ann.* 575, 174, 197 (1952).

where $x = 1, 2, 3, 4 \dots$

No addition products with the solvent, benzene or toluene, were reported. The data for the rate of decomposition of the N-nitrosolactams are tabulated:

Ring Size, n	Rate at 40° $k \times 10^7 \text{ sec}^{-1}$
5	0.00029
6	0.65
7	1540.
8	24200.
9	57500.
10	443.
11	157.

The nitrosolactam (a) passes partly at 20° into the cyclic diazoester (c) with the unimolecular speed of rearrangement passing through a maximum as ring size increases. Two factors influence this: (1) the bond system of the carbonyl carbon must become tetrahedral to pass through active intermediate (b). This is difficult in small lactam rings but becomes easier with increasing ring size; and (2) the trans form (d) of the possible configurations in open chain systems is favored due to electrical effects. In small lactam rings the geometry requires the cis form which is unfavorable for the formation of intermediate (b).

(d) trans

(e) cis

The decomposition of nitrosoamides was also studied as a method for the deamination of aliphatic amines;¹ the amines were acylated, the resulting amides nitrosated, and the nitrosoamides thermally decomposed to give esters, acids, and olefins. Data for this reaction are:

R	R'	solvent	Temp. °C	yields	
				%ester	%acid
n-Butyl	methyl	heptane	85	79	16
isobutyl	methyl	CCl ₄	77	62	37
sec-Butyl	methyl	CCl ₄	60	0	67
n-Butyl	3,5-dinitrophenyl	hexane	69	83	17
isobutyl	3,5-dinitrophenyl	hexane	69	66	33
sec-Butyl	3,5-dinitrophenyl	CCl ₄	30	26	59
sec-Butyl	phenyl	pentane	25	23	64
cyclohexyl	methyl	pentane	36	50	38
cyclohexyl	ethoxyl	CCl ₄	70	36	43
-Phenylethyl	methyl	pentane	36	35	0

The conversion of aliphatic amines into alcohols or their derivatives has not been widely practiced, since the deamination with nitrous acid, (the method usually used), furnishes poor yields of alcohols badly contaminated with by-products.² The decomposition of

1. E. White, J. Am. Chem. Soc. 77, 6008, 6011, 6014 (1955).

2. n-Butylamine was deaminated with sodium nitrite and hydrochloric acid to yield 25% of 1-butanol, 13% of 2-butanol, 37% of a mixture of 1- and 2-butenes, 5% of 1-chlorobutane, and 3% of 2-chlorobutane. F. C. Whitmore and D. F. Langlois, J. Am. Chem. Soc. 54, 344 (1932).

N-alkyl-N-nitrosoamides gives good yields of esters when the alkyl group was primary but gives poor yields when the alkyl group was secondary.

In conclusion, one can see that very little is known about the thermal decomposition of N-nitrosoamides, N-nitrosourethanes, and N-nitrosolactams.

PRESENT WORK

The compounds chosen for the thermal decomposition study were: 3-nitroso-5,5-diphenyl-2-oxazolidone, (IV), 3-nitroso-5-methyl-5-phenyl-2-oxazolidone, (V), and 3-nitroso-1-oxa-3-azaspiro[4.5]decan-2-one, (VI). The alkaline treatment of 3-Nitrosospiro[fluorene-9',5-oxazolidin]-2-one (VII), is discussed in a separate section.

IV

V

VI

VII

The preparation and properties of compounds IV, V, and VI have been previously described.¹

A. Thermal Decomposition

1. Experimental Method

The dry nitroso compound was placed in a dry flask, heated slowly to the proper temperature, and maintained at this temperature until the evolution of gas was complete. The volume of gas was measured over water.

When the decomposition was conducted in a solvent, the procedure was similar.

1. M. S. Newman and A. Kutner, J. Am. Chem. Soc. 73, 4199 (1951).

2. Identification of Products

The nature and yield of products are indicated in Table IV. In all cases, the parent oxazolidone was one of the products. A detailed discussion of pyrolysis products is given in Section 4. A brief description of the identification of the by-products obtained in the thermal decomposition of each nitroso compound follows.

3-Nitroso-5,5-diphenyl-2-oxazolidone

The by-products of the decomposition of this nitroso compound were found to be benzophenone, 1,1-diphenylethylene, and diphenylacetylene. On treatment of an aliquot of the reaction mixture with acidified 2,4-dinitrophenylhydrazine reagent,¹ the benzophenone derivative was obtained. When the filtrate from this derivative was refluxed with mercuric sulfate, desoxybenzoin 2,4-dinitrophenylhydrazone was obtained. The hydrocarbon fraction of the remaining reaction mixture, obtained by the use of chromatography, was submitted to multicomponent spectrophotometric analysis for 1,1-diphenylethylene and diphenylacetylene.

3-Nitroso-5-methyl-5-phenyl-2-oxazolidone

1. R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

Table IV

Products of Thermal Decomposition
No Solvents

R_1	R_2	Temperature	Products	Yields
ϕ	ϕ	185°	parent oxazolidone $\phi\phi\phi\phi$ $\phi_2C=CH_2$ $\phi CO\phi$	18% 32% a 40% a 6% b
ϕ	ϕ	168°	parent oxazolidone $\phi\phi\phi\phi$ $\phi_2C=CH_2$ $\phi CO\phi$	40% 23% a 26% a 6% b
ϕ	ϕ	153°	parent oxazolidone $\phi\phi\phi\phi$ $\phi_2C=CH_2$ $\phi CO\phi$	51% 20% a 21% a 5% b
ϕ	ϕ	120°	parent oxazolidone $\phi\phi\phi\phi$ $\phi_2C=CH_2$ $\phi CO\phi$	57% 16% a 15% a 5% b
ϕ	CH_3	185°	parent oxazolidone $\phi\phi\phi CCH_3$ $\phi C(CH_3)=CH_2$ $\phi COCH_3$ $\phi COCOCH_3$	50% 7% c 10% d 8% b 8% e

Table IV continued

R_1	R_2	Temperature	Products	Yields
$\emptyset$	CH_3	153°	parent oxazolidone $\emptyset\text{CCHCCH}_3$	64% 6% c
			$\emptyset\text{C}(\text{CH}_3)=\text{CH}_2$	5% d
			$\emptyset\text{COCH}_3$	7% b
			$\emptyset\text{COCOCH}_3$	6% e
--- $(\text{CH}_2)_5$ ---		185°	parent oxazolidone	57%
--- $(\text{CH}_2)_5$ ---		153°	parent oxazolidone	70%

- a. Estimated by multicomponent ultraviolet spectrophotometric analysis.
- b. On the basis of 2,4-dinitrophenylhydrazone formation.
- c. Estimated as 2,4-dinitrophenylhydrazone after hydration with sulfuric acid-mercuric sulfate.
- d. Estimated as 2,4-dinitrophenylhydrazone after ozonolysis.
- e. Estimated as osazone after hydration of the hydrocarbon fraction with sulfuric acid-mercuric sulfate.

The by-products of the decomposition of this nitroso compound were found to be acetophenone, α -methylstyrene, phenylmethylacetylene, and a compound presumed to be phenylallene. On treatment of an aliquot of the reaction mixture with acidified 2,4-dinitrophenylhydrazine reagent, the acetophenone derivative was obtained. When the filtrate from this derivative was refluxed with mercuric sulfate and sulfuric acid, two products were obtained: propiophenone 2,4-dinitrophenylhydrazone and the 2,4-dinitrophenylosazone of 1-phenylpropan-1,2-dione. The possible precursor, phenylallene, of this latter derivative will be discussed in a later section. The hydrocarbon fraction of the remaining reaction mixture, obtained by chromatography, was ozonized and the ozonide decomposed under reducing conditions. The acetophenone 2,4-dinitrophenylhydrazone obtained was used as a measure of the amount of α -methylstyrene originally present.

3-Nitroso-1-oxa-azaspiro[4.5]decan-2-one

The by-products of the decomposition of this nitroso compound were cyclohexanone and a considerable quantity of black tar. On treatment of an aliquot of the reaction mixture with acidified 2,4-dinitrophenylhydrazine reagent,¹ the cyclohexanone derivative

1. R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

was obtained.

Thermal Decomposition at 153° in the Presence of Solvents:

3-Nitroso-5,5-diphenyl-2-oxazolidone, IV, was decomposed in the following solvents: t-butylbenzene, nitrobenzene, methyl benzoate, perchloropropylene, bromobenzene, naphthalene, cumene, and p-xylene. In addition, 3-nitroso-1-oxa-3-azaspiro[4.5]decan-2-one and 3-nitroso-5-methyl-5-phenyl-2-oxazolidone were decomposed in certain solvents chosen from the above named group. These results are summarized in Table V. None of the solvents, except cumene and p-xylene, had an effect on the mode of decomposition of the nitroso compound. When cumene was used as a solvent, the yield of oxazolidone was greatly increased and the chief by-product was acetophenone. When p-xylene was used as a solvent, the yield of oxazolidone was also greatly increased and the chief by-product was p-toluic acid. Both of the by-products were probably formed from the solvent by nitric oxide oxidation.

3. Gas Analysis:

Quantitative gas analyses were obtained for the thermal decomposition of 3-nitroso-5,5-diphenyl-2-oxazolidone at 120° and 185° using a General Electric Analytical Mass Spectrometer. The pressure sensitivity technique¹ was used. The results of these analyses are shown in Table VI.

1. An example of the pressure sensitivity technique is described by R. A. Friedel, A. G. Sharkey, Jr., J. L. Shultz, and C. R. Humbert, *Anal. Chem.* 25, 1312 (1953).

Table V

Products of Thermal Decomposition in Solvents at 153°

R_1	R_2	Solvent	Products	Yields
$\emptyset$	$\emptyset$	none, t-butyl benzene, nitrobenzene, methyl benzoate, perchloro-propylene, bromobenzene, naphthalene	parent oxazolidone $\emptyset\text{C}\equiv\text{C}\emptyset$ $\emptyset_2\text{C}=\text{CH}_2$ $\emptyset\text{CO}\emptyset$	48-54% 18-20% a,b 21-22% b 5-6 % c
$\emptyset$	$\emptyset$	p-xylene	parent oxazolidone p-toluic acid	80% 18%
$\emptyset$	$\emptyset$	cumene	parent oxazolidone $\emptyset\text{COCH}_3$	(80% *(22% c
$\emptyset$	CH_3	none, nitrobenzene	parent oxazolidone $\emptyset\text{C}\equiv\text{CCH}_3$ $\emptyset\text{C}(\text{CH}_3)=\text{CH}_2$ $\emptyset\text{COCH}_3$ $\emptyset\text{COCOCH}_3$	61-64% 6-7 % a ----- 7% c 6% d
$\emptyset$	CH_3	cumene	parent oxazolidone $\emptyset\text{COCH}_3$	88% 28% c
-----(CH_2) ₅ ----		none, nitrobenzene, methyl benzoate	parent oxazolidone cyclohexanone	66-70% 1-2 % c
-----(CH_2) ₅ ----		cumene	parent oxazolidone $\emptyset\text{COCH}_3$	90% 41% c

Table V (continued)

- a. Estimated as a 2,4-dinitrophenylhydrazone; after hydration with sulfuric acid-mercuric sulfate.
- b. Estimated by multicomponent ultraviolet spectrophotometric analysis.
- c. On the basis of 2,4-dinitrophenylhydrazone formation.
- d. Estimated as 2,4-dinitrophenylosazone, after hydration of hydrocarbon fraction with sulfuric acid-mercuric sulfate.
- * Average of five determinations.

Table VI

Mass Spectrometric Gas Analysis of
Gases from the Thermal Decomposition
of 3-Nitroso-5,5-diphenyl-2-oxazolidone

Product	Moles product per Mole nitroso compound	
	●185°	●120°
H ₂ O	0.25	0.08
N ₂	0.35	0.40
NO	0.05	0.04
N ₂ O	0.53	0.31
CO ₂	0.87	0.53
oxazolidone	0.18	0.57
ϕ ₂ C=CH ₂	0.40	0.15
HC≡CH	0.32	0.16
ϕ ₂ C=O	0.06	0.05
unidentified	0.04	0.07

4. Correlation of Results:

Electronic Considerations

The 2-oxazolidones may be saponified by α -amino alcohols by refluxing in alkali, or hydrolyzed by treating with cold, concentrated hydrochloric acid.¹ At room temperature, however, the oxazolidones are quite stable to the action of alkali, dilute acid, or heat.² However, when a nitroso group is introduced at the 3-position, a great change occurs in the reactivity of the molecule. This great change may be attributed to the electrophilic character of the nitroso group.^{3,4} The inductive effect of this group must be strong enough to increase the polarization of the carbonyl group. Thus the carbonyl group not only becomes much more susceptible to the attack of nucleophilic reagents^{5,6} but also more susceptible to homolytic split. We will not consider this homolysis in detail.

Possible Reaction Paths

a. General Scheme

The mechanism which we favor for the thermal decomposition of 5-substituted 3-nitroso-2-oxazolidones are presented in Chart I.

-
1. R. Baltzly and J. S. Buck, J. Am. Chem. Soc. 62, 164 (1940).
 2. 5,5-diphenyl-2-oxazolidone was found to be stable for six hours at 225°. cf. EXPERIMENTAL, Section A, part 5.
 3. D. L. Hammick, R. G. A. New, and L. E. Sutton, J. Chem. Soc. 742 (1932).
 4. A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Ed., John Wiley and Sons, 1949, p. 362.
 5. M. S. Newman and A. Kutner, J. Am. Chem. Soc. 73, 4199 (1951).
 6. M. S. Newman and W. A. Edwards, J. Am. Chem. Soc. 76, 1840 (1954).

Chart I

Mechanism for the Thermal Decomposition of 5-substituted
3-nitroso-2-oxazolidones

The 5-position has two substituents, R and R', where R and R' are phenyl or alkyl. The steps of the mechanism presented form a logical path, but not necessarily the only path, to the final products. This scheme is as follows:

Route (1): The nitroso compound, VIII, undergoes homolytic cleavage of the nitrogen-nitrogen bond to yield nitric oxide and the oxazolidyl radical, IX.¹ Radical IX abstracts an hydrogen atom to give the parent oxazolidone, X. The source of this hydrogen atom is unknown. The hydrogen may come from the starting material, an intermediate, or from one of the products of the decomposition. We believe that the tar obtained arises from the fragments produced by hydrogen abstraction.

Route (2): The nitroso compound, VII, undergoes electronic shifts leading directly to 1,1-diphenylethylene, XI, nitrous oxide, and carbon dioxide.

Route (3): The nitroso compound, VIII, undergoes a hydride shift through a concerted mechanism resulting in ring cleavage to give XII²

1. N-Nitrosopyrrolidone upon heating undergoes homolytic cleavage of the nitrogen-nitrogen bond. The gaseous products of this decomposition were nitric oxide (54%) and nitrogen (46%). R. Huisgen and J. Reinertshofer, Ann. 575, 197 (1952).
2. Structure XII can also arise through a homolytic cleavage of the carbon-nitrogen bond to give XVII, which undergoes a 1,2-hydrogen shift to XVIII. Electronic shifts give XII and carbon dioxide.

and carbon dioxide. Structure XII is converted to its tautomeric form, the diazohydroxide, XIII, which is itself in resonance with form XIV.¹ Migration of a phenyl group² gives nitrogen and carbonium ion XV which is stabilized by the loss of a β -hydrogen to give XVI.³

We did not consider ring expansion as a likely route of decomposition on the basis of the behavior of N-nitrosolactams under the same conditions. Due to the small ring size of 3-nitroso-2-oxazolidones the carbonyl and nitroso groups are in the cis form which is unfavorable for the formation of intermediate XIX.⁴

There is no direct evidence in favor of the proposed mechanism. The cleavage of the nitrogen-nitrogen bond is undoubtedly a homolytic one; however, what happens after that is speculative. We thought that Gomberg-like products could be obtained by thermally decomposing

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1. This nitroso-diazohydroxide system is very mobile. C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 583.
 2. Observed only when R or R' is phenyl.
 3. The steps involved in the sequence XIV, XV, and XVI were proposed by M. S. Newman and A. Kutner, J. Am. Chem. Soc. 73, 4199 (1951).
 4. See BACKGROUND for details of the thermal decomposition by ring expansion of the N-nitrosolactams. Also note, R. Huisgen and J. Reinertshofer, Z. Naturforsch. 6B, 395 (1951).

3-nitroso-5,5-diphenyl-2-oxazolidone¹ in aromatic solvents if the decomposition was taking place by a free radical mechanism.

b. Effect of Solvents:

The thermal decomposition of 3-nitroso-5,5-diphenyl-2-oxazolidone, IV, in the presence of solvents was conducted conveniently at the intermediate temperature of 153°, since at 120° the decomposition was very slow and at 220° the decomposition was explosive. When IV was decomposed in the solvents t-butylbenzene, nitrobenzene, methyl benzoate, perchloroethylene, bromobenzene, and naphthalene, no change in the mode of decomposition was observed.² When 3-nitroso-5-methyl-5-phenyl-2-oxazolidone, V, and 3-nitroso-1-oxa-3-azaspiro [4.5] decan-2-one, VI, were decomposed at 153° in selected solvents² of the preceding group, no change in the mode of decomposition was observed. The decomposition may be taking place in a "solvent cage" thus minimizing attack upon the solvent.

The only solvents which significantly altered the ratio of decomposition products of the 3-nitroso-2-oxazolidones, were p-xylene and cumene. Both of these solvents have benzyl hydrogens which were easily abstracted by the oxazolidyl radical, IX. In such solvents, the yield of oxazolidone was 80-90%. The mechanism is shown using cumene as the solvent.

1. Chosen for this study since the thermal decomposition in the absence of a solvent yielded less tar than the other nitroso compounds investigated.

2. See Table V.

The nitroso compound upon heating yields the oxazolidyl radical IX. An hydrogen atom is abstracted from cumene to give the oxazolidone X and a new radical, XXI, which is eventually oxidized to acetophenone and small amounts of methanol and acetone.¹ No dimer of radical XXI, 2,3-dimethyl-2,3-diphenylbutane was found. The appearance of acetophenone as a product which must have come from cumene, the solvent, led us to a brief study of the oxidation of hydrocarbons by nitric oxide.

c. Oxidation by nitric oxide

Nitric oxide was bubbled through cumene at 153° under a nitrogen atmosphere. The products were acetophenone and small amounts of methanol and acetone. The infrared spectrum indicated traces of nitro compounds. These results showed that the 3-nitroso-2-oxazolidones were not necessary for the production of acetophenone.

There is little information in the literature concerning the reaction of nitric oxide with saturated hydrocarbons below 400-600°. Oxidation by nitric oxide gives nitrous oxide and nitrogen as the products.² Other scattered references in the literature state that

1. See Table V.

2. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Volume 8, Longmans, Green, and Co., London, England, 1928, p. 384.

there is some interaction between nitric oxide and substances such as turpentine,¹ rubber solutions, ^{2,3} cyclohexene,² gaseous dienes,⁴ and styrene;⁵ however no products were identified. It has also been reported that nitrous oxide acts as an oxidizing agent toward hydrocarbons only at temperatures of 400-500° and above.⁶

From a private communication,⁷ it was learned that cumene was oxidized with nitric oxide at 80° and 250 psig. to yield

Unidentified nitro compound	3%
Acetophenone	12%
2-Phenyl-2-propanol	10%
2-Phenyl-2-nitropropane	14%
α -(Nitromethyl)styrene	12%
α -Methyl- β -nitrostyrene	10%
1-Nitro-2-phenyl-2-propanol	7%
Residue	22%

A trace of nitrogen dioxide is necessary before oxidation will occur. Benzene was inert to nitric oxide at 120° and 200 psig. Tertiary butylbenzene reacted slowly with nitric oxide at 100° and 200 psig.

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1. T. Panzer, Z. physiol. chem. 93, 378 (1925).
 2. G. F. Bloomfield and G. A. Jeffrey, J. Chem. Soc. 120 (1944).
 3. A. Gorgas, Ber. 63, 2700 (1930).
 4. N. B. Biggs, Gas J. 235, 213 (1941); W. H. Fulweiler, Am. Gas J. 142, 27 (1935).
 5. J. C. Devins and C. A. Winkler, Can. J. Research, 26B, 356 (1948).
 6. F. S. Bridson-Jones, G. D. Buckley, L. H. Cross, and A. P. Driver, J. Chem. Soc. 2999, 3009, 3016 (1951).
 7. J. F. Brown, Jr., and C. A. Burkhard, General Electric Company, Schenectady, New York.

but the analysis of the products was qualitative. The following, involving both free radical and ionic mechanisms, was proposed.

(R is alkyl or aryl)

It is doubtful that all of the preceding mechanism applies to the oxidation of cumene or p-xylene during the thermal decomposition of 3-nitroso-2-oxazolidones because the nitric oxide concentration must be much less than one atmosphere.

d. 3-Nitroso-5,5-diphenyl-2-oxazolidone:

IV

The products of the thermal decomposition of nitroso compound IV, 5,5-diphenyl-2-oxazolidone, diphenylacetylene, 1,1-diphenylethylene, and benzophenone can be explained by the proposed mechanism in part a. Because the phenyl group is resistant to oxidation by nitric oxide,¹

1. J. F. Brown, Jr., and C. A. Burkhard, General Electric Company, Schenectady, New York, private communication.

only two hydrogens are available in nitroso compound IV, (neglecting the water formed in oxidation), to the oxazolidyl radical IX; therefore, tar formation is kept at a minimum. Yet oxidation by nitric oxide occurs as shown by the comparison of the mass spectrometric gas data with the theoretical gas analysis.¹ At 185°, these data are:

<u>moles gas</u> <u>mole nitroso compound</u>	H ₂ O	N ₂	NO	N ₂ O	CO ₂	Total
moles of gas (mass analysis)	0.25	0.35	0.05	0.53	0.87	2.05
moles of gas (theoretical)	0.32	0.32	0.18	0.50	0.82	2.14

At 120°, these data are:

<u>moles gas</u> <u>mole nitroso compound</u>	H ₂ O	N ₂	NO	N ₂ O	CO ₂	Total
moles of gas (mass analysis)	0.08	0.40	0.04	0.31	0.53	1.36
moles of gas (theoretical)	0.16	0.16	0.57	0.28	0.44	1.51

Benzophenone was assumed to be the result of the oxidation of

1. The theoretical gas analysis is based on these reactions:

1,1-diphenylethylene¹ or its precursors. Since nitric oxide is the oxidizing agent, and not nitrous oxide,² the oxidation may take place as follows:

Both the data at 185° and at 120° show that much less nitric oxide is present than one might expect from theory. Also, at 120°, there is less nitrogen found than one might expect. However, if the oxidation is taken into consideration, the overall effect is that the amounts of nitrogen, nitrous oxide, carbon dioxide increase and the amount of nitric oxide decreases. Then the amounts of gases calculated on the basis of the mechanism (part a) and the oxidation agree more closely with the analytical data.

In order to see if diphenylacetylene came from 1,1-diphenylethylene, nitroso compound IV was thermally decomposed in excess 1,1-diphenylethylene. The fact that no diphenylacetylene was obtained proved that the diphenylacetylene did not come from 1,1-diphenylethylene. In this experiment, 87% of the parent oxazolidone was obtained. Thus the 1,1-diphenylethylene behaves as a solvent comparable to cumene and p-xylene as a hydrogen donor.

A striking temperature effect is exhibited on the amounts of each product in the thermal decomposition of nitroso compound IV.³

1. Substantiated by experiment.

2. F. S. Bridson-Jones, G. D. Buckley, L. H. Cross, and A. P. Driver, J. Chem. Soc. 2999, 3009, 3016 (1951).

3. See Table IV.

The amount of oxazolidone obtained decreases as the decomposition temperature increases and the amounts of diphenylacetylene and 1,1-diphenylethylene increase as the decomposition temperature increases. Therefore, Route (1) is energetically favored over Routes (2) and (3) at low temperatures but at high temperatures the latter Routes become more significant.

e. 3-Nitroso-5-methyl-5-phenyl-2-oxazolidone

The products of the thermal decomposition of nitroso compound V are the parent oxazolidone, acetophenone, α -methylstyrene, phenylmethylacetylene, and an unknown compound. All of the products except the unknown product are explained by the mechanism proposed in part a of this Section.

We have evidence that the unknown compound is phenylallene. The appearance of phenylallene in the products may be pictured as follows:

The transformations between intermediates XXV and XXVII are

explained in part a, this Section.¹

The chief evidence in favor of phenylallene is the formation of the 2,4-dinitrophenylosazone of 1-phenylpropan-1,2-dione upon hydration of a hydrocarbon fraction of the decomposition products with mercuric sulfate, sulfuric acid, and 2,4-dinitrophenylhydrazine. The hydration of phenylallene to 1-phenylpropan-1,2-dione with mercuric salts is known.²

Phenylacetone, treated with mercuric sulfate and sulfuric acid, gives a high yield of 1-phenylpropan-1,2-dione, but no phenylacetone was present in the thermal decomposition reaction mixture as shown by the fact that acetophenone was the only carbonyl compound present. Furthermore, the glycol XXX³ does not lead to phenylacetone since the following is known to occur.⁴

Propiophenone and phenylmethylacetylene treated with mercuric sulfate and sulfuric acid both gave a low yield of the diketone.

1. c.f. Chart I, (intermediates XII through XV).
2. M. Bourguet, Compt. rend. 192, 686 (1931).
3. Although the cyclic carbonate was considered as an unlikely thermal decomposition product, it was not conclusively excluded, (part a, this section). Hydrolysis of the cyclic carbonate would lead to glycol XXX.
4. M. Tiffeneau, Ann. chim. [8], 10, 343 (1907).

However, only one-tenth of the observed diketone could be accounted for in this way. Therefore, we favor phenylallene as the 1-phenylpropan-1,2-dione precursor.

f. 3-Nitroso-1-oxa-3-azaspiro[4.5]decan-2-one

The products of the thermal decomposition of nitroso compound VI are the parent oxazolidone and a large amount of tar. The oxazolidone is explained by the mechanism proposed in part a of this Section. At a decomposition temperature of 185°, 57% of the parent oxazolidone was obtained. It is likely that the pentamethylene substituent is not only a ready source of hydrogen atoms for the oxazolidyl radical but is also easily oxidized by nitric oxide.¹

B. Alkaline Decomposition

1. Preparation of 3-Nitrosospiro[fluorene-9',5-oxazolidin]-2-one

The Nitroso compound VII was prepared by a known sequence of reactions:² a Curtius rearrangement of a β -hydroxy acid azide

1. Cyclohexane reacts with nitric oxide at 120° and 200 psig to give cyclohexanone, cyclohexanol, and nitrated cyclohexanes. Private communication from J. F. Brown, Jr., and C. A. Burkhard, General Electric Company, Schenectady, New York.
2. M. S. Newman and A. Kutner, J. Am. Chem. Soc. 73, 4199 (1951).

followed by nitrosation.

The synthesis involved several steps: a Reformatsky reaction between fluorenone and methyl α -bromo acetate, formation of the acid hydrazide from the resulting ester by reaction with anhydrous hydrazine followed by nitrous acid treatment to convert the hydrazide to the azide. The azide was thermally decomposed in the presence of petroleum ether, boiling range 55-70° (Skellysolve B), the violence of the decomposition being spent by the boiling Skellysolve. The desired 2-oxazolidone in anhydrous pyridine, was nitrosated in 90% yield by the addition of an acetic anhydride solution of nitrosyl chloride. The nitroso compound was isolated by dilution with water. This sequence is outlined in Chart II.

2. Properties of 3-Nitrosospiro[fluorene-9',5-oxazolidin]-2-one, VII

Nitroso compound VII crystallized readily from a benzene-petroleum ether mixture as light yellow needles, m.p. 165° dec. Under refrigeration the compound was stable for months, but at room temperature the odor of nitrous fumes was evident after one week.

3. Decomposition of 3-Nitrosospiro[fluorene-9',5-oxazolidin]-2-one, VII, with Alkali

a. Experimental Method

One part of nitroso compound VII was mixed with ten parts of methanol in a flask. One equivalent of 50% potassium hydroxide was added dropwise. The nitrogen evolved¹ was measured over water. The reaction mixture was diluted with water and extracted with benzene.

1. One mole of nitrogen was evolved per mole of nitroso compound VII.

CHART II

PREPARATION OF 3-NITROSOSPIRO [FLUORENE -9',5-OXAZOLIDIN]-2-ONE

The combined benzene extracts were concentrated in the dark, placed on a column packed with alumina, and developed with benzene. The first fraction yielded 87% of pure 9-(methoxymethylene)fluorene, XXXII.

XXXII

A trace of an iodine colored solid, which could not be identified, was obtained from the second fraction.

b. Possible Reaction Path

The mechanism proposed by Newman and Kutner¹ explains the major product of the decomposition of nitroso compound VII. The first step of this reaction probably involves the cleavage of XXXIII to XXXIV

followed by a tautomeric shift to XXXV. The base catalyzed removal of carbonic acid gives rise to diazohydroxide XXXVI which loses nitrogen and hydroxyl ion to give the carbonium ion XXXVII. In the alkaline decomposition of nitroso compound VII, carbonium ion XXXVII is seen as

1. M. S. Newman and A. Kutner, J. Am. Chem. Soc. 73, 4199 (1951).

XXXVIII. Carbonium ion XXXVIII may react directly with the solvent

to give XXXII or undergo rearrangement to XXXIX before reacting with solvent to give XL. It is interesting that 9-(hydroxymethyl)fluorene, XLI, upon refluxing with phosphorus pentoxide in xylene, gives phenanthrene in high yield.¹ A significant difference is apparent

between ions XXXVIII and XLII: the unsaturated carbonium ion yields an unrearranged product and the saturated carbonium ion yields a rearranged product. The fact that no phenanthrene derivative is formed is good evidence that the mechanism proposed by Newman and Kutner is valid since XXXV can decompose by way of XXXVI (loss of carbonic acid) or by loss of hydroxyl ion and nitrogen to give ion XLIV,

1. W. G. Brown and B. Bluestein, J. Am. Chem. Soc. 62, 3256 (1940).

which is similar to XLII and could be expected to rearrange to give the phenanthrene derivative and hydrogen ion or the cyclic carbonate XLVII. Because XLV and XLVI are not among the products, initial loss of nitrogen and hydroxyl ion probably do not occur. However, it must be pointed out that one fallacy exists in this reasoning: namely, the loss of a proton from XLIV to give the carbene XLVII which rearranges by the loss of bicarbonate ion to give intermediate

XXXVII. This path of decomposition thus can give the same unsaturated carbonium ion as the mechanism proposed by Newman and Kutner.

SUGGESTIONS FOR FURTHER WORK

A rearrangement has been shown to take place in the thermal decomposition of 5-substituted-3-nitroso-2-oxazolidones but the mechanism is a matter of conjecture. Should the nitroso derivatives of 4,5,5-triphenyl-, 4,4,5-triphenyl-, and 4,4,5,5-tetraphenyl-2-oxazolidones be thermally decomposed, the reaction mixtures should become simpler since no acetylene can be formed without rupture of a carbon-carbon bond. The tetraphenylated nitroso compound should give tetraphenylethylene in high yield in which case a kinetic study of the decomposition could be made. A series of compounds substituted in the 4-position alone also bears investigation.

It might also be interesting to treat some substituted 2-oxazolidones with N-bromosuccinimide or N-bromophthalimide. This reaction might lead to the generation of oxazolidyl radicals without introducing the complications of oxidation and free radical trapping by nitric oxide which occur in the thermal decomposition of 5-substituted 3-nitroso-2-oxazolidones. In addition, the 2-oxazolidones might undergo decomposition in the presence of peroxides such as t-butyl peroxide.

EXPERIMENTAL

All melting points up to 200° were taken using calibrated Anschütz total immersion thermometers. Melting points over 200° were taken on an electrically heated melting point block and are not corrected.

Analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Freshly prepared 2,4-dinitrophenylhydrazine solution was used to analyze for aldehydes and ketones.¹ A small excess of this reagent was refluxed for a few minutes with an ethanol solution of the carbonyl compound and the mixture cooled for at least four hours. The precipitate was chromatographed on a short column packed with alumina and developed with benzene. This treatment removed unreacted 2,4-dinitrophenylhydrazine and sulfuric acid.

All solid compounds were compared to an authentic sample by mixed melting point and by infrared spectra of the Nujol mulls.

Unless otherwise stated, all per cent yields are on the basis of the nitroso oxazolidone used.

1. R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

A. 3-Nitroso-5,5-diphenyl-2-oxazolidone,¹ IV 1. Decomposition in the Absence of a Solvent at 185°

The solid nitroso compound (10.33 g., 0.0385 mole) was placed in a previously dried 100 ml. flask connected to a gas collecting device. The flask was heated slowly in a salt bath until a temperature of 185-190° had been reached and maintained at that temperature until the evolution of gas had ceased (usually thirty to forty minutes). The decomposition was active but never violent.

After cooling, 12 ml. of petroleum ether (30-60°) and 2.5 ml. of ethanol were added and the material thoroughly mixed. The solid obtained was recrystallized from ethanol to yield 5,5-diphenyl-2-oxazolidone, (0.89 g.), m.p. 199-201°.¹

The filtrate was evaporated to give 6.38 g. of a pale yellow oil A which was treated as follows. A portion of A (0.52 g.) was treated with excess 2,4-dinitrophenylhydrazine solution. Benzophenone 2,4-dinitrophenylhydrazone, (0.069 g., 6.1%), m.p. 238-239°, ² was obtained. The filtrate, containing oil A and unreacted reagent, was refluxed one hour with 2 g. of mercuric sulfate and 5 ml. of sulfuric acid and then

1. M. S. Newman and A. Kutner, J. Am. Chem. Soc. 73, 4199 (1951). 5,5-diphenyl-2-oxazolidone, m.p. 199.6-200.4°.
2. E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Volume I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 363, gives melting point 238-239°.

cooled. Desoxybenzoin 2,4-dinitrophenylhydrazone, (0.331 g., 28.1 %), m.p. 202-203⁰¹ was obtained. (Pure diphenylacetylene was converted to desoxybenzoin 2,4-dinitrophenylhydrazone in 85% yield using the above technique).

Another portion of the oil A (5.38 g.) was dissolved in 3 ml. chloroform and 3 ml. petroleum ether (55-70⁰) and chromatographed on a 5.6 x 19 cm. column packed with silicic acid, and developed with 5% ether in petroleum ether. The first fraction eluted B (4.66 g.) was shown by infrared spectrum to be a mixture of hydrocarbons and benzophenone. The second fraction, 0.64 g., was the parent 5,5-diphenyl-2-oxazolidone; when this was combined with the crystalline material from the original reaction mixture, 1.65 g. (17.9%) of the oxazolidone were obtained. The third fraction, 0.06 g., was a black tar and could not be identified.

The first fraction B was rechromatographed (as in the above paragraph) to yield a colorless oil C (4.30 g.) whose infrared spectrum showed it to be solely hydrocarbon, and a pale yellow oil D (0.35 g.) whose infrared spectrum was identical with that of an authentic sample of benzophenone. From D was made 0.691 g. (5.9%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 238-239⁰. This checked well with the previous determination, (6.1%).

The rechromatographed hydrocarbon oil C was treated in four ways to determine the composition: (1) A portion of C (0.482 g.) was

1. E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Volume I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 365, gives melting point 204⁰.

treated with excess 2,4-dinitrophenylhydrazine solution, but, after cooling, no carbonyl derivative was obtained. This solution was then refluxed with 2 g. mercuric sulfate and 5 ml. sulfuric acid and then allowed to cool. After workup desoxybenzoin 2,4-dinitrophenylhydrazone, (0.377 g., 27.5 %), m.p. 202-203°, was obtained.

(2) A portion of oil C (0.632 g.) was ozonized.^{1,2} During the early stages of this ozonolysis a carbonyl derivative was obtained by passing the exit gases through 2,4-dinitrophenylhydrazine reagent. This solid, 0.0216 g., was found to be the formaldehyde derivative, m.p. 164-165°.³ The acid fraction from the ozonolysis yielded benzoic acid, (0.107 g.), m.p. 120-121°.⁴ The neutral fraction from the ozonolysis was treated in the usual manner to yield benzophenone 2,4-dinitrophenylhydrazone (0.547 g.), m.p. 239-240°. This means that at least 43% of the hydrocarbons are unsymmetrically substituted.

(3) A portion of oil C (0.263 g.) was treated with an excess of 2,4-dinitrobenzenesulfonyl chloride in glacial acetic acid containing a small amount of acetic anhydride, heated for thirty minutes on a steam bath, poured onto ice and water, and extracted with benzene. The benzene solution was chromatographed, according to Lee,⁵ to give

1. J. Doeuvre, Bull. soc. chim. [5] 3, 612 (1936).

2. E. Briner and D. Frank, Helv. Chim. Acta. 22, 591 (1939).

3. E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 50, gives melting point 166°.

4. Ibid, p. 146, gives melting point 121.4°.

5. G. H. Lee, M. S. Dissertation, The Ohio State University, 1954.

1,1-diphenyl-2-(2,4-dinitrobenzenesulfonyl)ethylene, (0.179 g.),
m.p. 135.5-136.5°. ¹ (An authentic sample was prepared according to
Kharasch and coworkers.) ^{1,2}

(4) A sample of oil C was submitted to multicomponent ultra-violet spectrophotometric analysis similar to one used by Tunnicliff et al. ³ Pure samples of 1,1-diphenylethylene ⁴ and diphenylacetylene ⁵ were prepared and used as reference compounds (Figure I). Several wave lengths were used for the determinations but 2500A and 2700A were the two wavelengths found to give the most reproducible results. A typical analysis is described: A solution was prepared in absolute ethanol containing 1.062×10^{-3} g. oil/100 ml. The data for a sample calculation follow:

The equations used were:

$$(1) \quad A_{2500} = XE_1 + YE_3$$

$$(2) \quad A_{2700} = XE_2 + YE_4$$

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1. N. Kharasch and C. M. Buess, J. Am. Chem. Soc. 71, 2724 (1949) give melting point 135.5-136.5°.
 2. No adduct is formed with acetylenes when a catalytic amount of anhydrous aluminum chloride is present. N. Kharasch and S. J. Ascony, J. Am. Chem. Soc. 75, 1081 (1953).
 3. D. D. Tunnicliff, R. R. Brattain, and L. R. Zumwalt: Anal. Chem. 21, 890 (1949).
 4. C. F. H. Allen and S. Converse in "Organic Synthesis," Collective Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 226.
 5. L. I. Smith and M. M. Falkof in "Organic Syntheses," Vol. 22, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 50.

FIG. 1. ULTRAVIOLET SPECTRA FOR DIPHENYLACETYLENE, ($\phi C \equiv C \phi$), AND 1,1-DIPHENYLETHYLENE, ($\phi_2C=CH_2$), IN ETHANOL, $7.00 \times 10^{-4} \text{ g/100 ml}$.

where A_{2500} is the optical density at 2500 Å

A_{2700} is the optical density at 2700 Å

l is the cell length (1.00 cm.)

E_1 and E_2 are the extinction coefficients of diphenylacetylene at 2500 and 2700Å, respectively, calculated with the concentration in g./100 ml.

E_3 and E_4 are the extinction coefficients of 1,1-diphenylethylene at 2500 and 2700Å, respectively, calculated with the concentration in g./100 ml.

X is the concentration of diphenylacetylene in g./100 ml.

Y is the concentration of 1,1-diphenylethylene in g./100 ml.

The data are

$$A_{2500} = 0.766$$

$$A_{2700} = 0.765$$

$$E_1 = 634$$

$$E_2 = 1225$$

$$E_3 = 808$$

$$E_4 = 336$$

Substitution in equations (1) and (2) yields

$$0.766 = 634X + 808Y$$

$$0.765 = 1225X + 336Y$$

Solving for X and Y

$$X = 0.463 \times 10^{-3} \text{ g./100 ml.}^1$$

$$Y = 0.584 \times 10^{-3} \text{ g./100 ml.}^1$$

$$X + Y = 1.047 \times 10^{-3} \text{ g./100 ml.}$$

1. Using the extinction coefficients measured at 2350 and 2800Å
 $X = 0.462 \times 10^{-3} \text{ g./100 ml.}$ and $Y = 0.592 \times 10^{-3} \text{ g./100 ml.}$

The actual sample concentration was compared to 1.062×10^{-3} g./100 ml. In terms of the entire hydrocarbon fraction, 2.23 g. (32.4%) of the reaction mixture was diphenylacetylene and 2.81 g. (40.3%) of the reaction mixture was 1,1-diphenylethylene.

The dry gas collected (1559 ml., S.T.P.) was more than theory (866 ml.); this was 1.80 moles of gas/mole of nitroso compound. A sample of this gas when shaken with ammonical silver hydroxide gave no metallic silver,¹ denoting the absence of carbon monoxide.

Quantitative Gas Analysis

The Gas analyses were run by mass spectrometric methods.

Apparatus:

(1) The mass spectrometer used was a General Electric Analytical Mass Spectrometer.

(2) The sampling device consisted of an all glass system built with vacuum stopcocks, a trap used to freeze out organic materials, a manometer (0-130 mm. Hg), a decomposition vessel of 50 ml. capacity, and a gas sample bulb of 50 ml. capacity.

Materials Used:

(1) Nitric Oxide and Nitrous Oxide were used from the cylinders supplied by The Matheson Co., Inc., East Rutherford, New Jersey.

(2) Helium was used from the cylinders supplied by Air Reduction Company.

(3) Carbon dioxide was obtained by pumping on a small piece of dry ice in a thimble cooled in liquid air, removing the liquid air

1. G. Lunge and H. R. Ambler, "Technical Gas Analysis," Curney and Jackson, London, 1934, p. 228.

bath, and finally allowing the carbon dioxide to sublime into the sample manifold of the spectrometer.

Procedure:

The pressure sensitivity technique¹ was used. The pressure sensitivities of all of the individual gases were determined by introducing a fixed volume of each gas into the manifold and reading the pressure on a manometer. The background, caused by residuals in the instrument, was determined prior to the running of each gas sample. These backgrounds were subtracted from their respective sample values before any calculation was attempted. It was necessary also to determine the cracking patterns of all of the gases used. These cracking patterns were determined simultaneously with the pressure sensitivities.

A typical sensitivity and cracking pattern was run as follows: A sample of air under 39.0 mm. pressure was introduced to the sample manifold. The background was run followed by the sample. (Air was considered to be 78% nitrogen by volume).² The connection in the mass peak height due to carbon dioxide was too small to be significant in an air sample (c.f. Table VII). The most intense peak for nitrogen was at mass 28 and the sole contributing factor of the nitrogen cracking pattern was at mass 14. (None of the other constituents of air

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1. For an example of this technique, see: R. A. Friedel, A. G. Sharkey, Jr., J. L. Shultz, and C. R. Humbert, *Anal. Chem.* 25, 1312 (1953).
 2. "Handbook of Chemistry and Physics," 35th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1953, p. 3086, gives 78.03% nitrogen by volume for dry air.

Table VII

Sensitivities and Cracking Patterns

Air: 39.0 mm.

m/e mass	Background units	Sample Peak Height units	Corrected Peak Height units
12 ⁺	-----	-----	-----
14 ⁺	-----	22.2	22.2
16 ⁺	0.4	7.0	6.6
18 ⁺	3.1	3.8	0.7
28 ⁺	62.1	458.	396.
29 ⁺	-----	2.0	2.0
32 ⁺	9.6	82.0	72.4
40 ⁺	-----	7.5	7.5
44 ⁺	0.5	1.8	1.3

CO₂: 38.0 mm.

12 ⁺	-----	29.5	29.5
22 ⁺	-----	4.1	4.1
28 ⁺	70.9	100.7	29.8
44 ⁺	1.1	406.	405.

N₂O: 22.6 mm.

14 ⁺	2.9	12.7	9.8
28 ⁺	66.1	96.9	30.8
30 ⁺	-----	57.4	57.4
44 ⁺	3.1	177.4	174.3

NO: 17.0 mm.

14 ⁺	1.8	11.4	9.6
28 ⁺	64.5	75.0	8.5
30 ⁺	0.5	218.	218.

H₂O: 4.2 mm.

18 ⁺	3.0	21.6	18.6
-----------------	-----	------	------

can have fragments of mass 14.) The ratio of the peak height of mass 14 to that of mass 28 was calculated since nitrous and nitric oxides have the same fragments at mass 14:

$$\frac{14^+}{28^+} = \frac{6.6}{396} = 0.0560 \text{ (relative peak intensity)}$$

The pressure sensitivity factor, k_{N_2} , was calculated:

$$(39.0)(0.78) = 31.0 \text{ mm. partial pressure nitrogen}$$

$$396 \text{ units} = \text{observed intensity (peak height at mass 28)}$$

$$\text{then } k_{N_2} = \frac{396}{31.0} = 12.8 \text{ divisions/mm.}$$

In the same manner, the pressure sensitivities and cracking patterns for all of the other gases were determined:

RELATIVE PEAK INTENSITIES

m/e mass	CO ₂	N ₂ O	NO	N ₂	H ₂ O
44 ⁺	1.00	1.00	-----	-----	-----
30 ⁺	-----	0.329	1.00	-----	-----
28 ⁺	0.0736	0.177	0.0863	1.00	-----
22 ⁺	0.0101	-----	-----	-----	-----
18 ⁺	-----	-----	-----	-----	1.00
14 ⁺	-----	0.0562	0.0441	0.0560	-----
12 ⁺	0.0729	-----	-----	-----	-----
$k \left(\frac{\text{div}}{\text{mm.}} \right)$	10.7	7.72	13.2	12.8	4.43

A mixture of gases which contained nitrous oxide and carbon dioxide could not be resolved by a direct measurement; therefore, two measurements were made using two different samples. One sample was taken as described previously. The second gas sample was collected through an 8 x 150 mm. Ascarite¹ tube which absorbed the carbon

1. Registered trade mark of Arthur H. Thomas Company, Philadelphia, Pa. Ascarite is a sodium hydrate-asbestos absorbent prepared according to J. B. Stetser and R. H. Horton, Iron Age, 102, 443 (1918)

dioxide and some water. Samples of nitrous and nitric oxides, placed in the isolated gas system containing the Ascarite tube, were not affected during a twenty-four hour period.

A typical sampling is described: The nitroso compound, (0.32 g.), was placed in a clean, dry reaction bulb. The system was evacuated and then filled with helium. The evacuation and helium filling was repeated five times. The system was isolated and a salt bath, heated to 185°, was placed about the reaction bulb. Reaction was lively. The pressure within the system increased to 135 mm. in twenty-five minutes and then remained constant. After forty minutes at 185°, the salt bath was removed and the gas sample bulb removed from the system.

A second sample of the nitroso compound, 0.350 g., was placed in a clean, dry reaction bulb. The Ascarite tube was inserted between the sample bulb and the rest of the apparatus. Decomposition was accomplished as before. The final pressure was 105 mm.

Calculation:

The sample which did not contain carbon dioxide was used to calculate the ratio $44^+/30^+$. Nitrous oxide and nitric oxide were the only two components which contributed to mass 30. In this sample, nitrous oxide was the only component contributing to mass 44. Even if carbon dioxide were present, this ratio remained the same. When the ratio $44^+/30^+$ was multiplied by the peak height at mass 30 in the sample which contained carbon dioxide, the result was the peak height at mass 44 due to nitrous oxide. The remainder of the mass 44 peak height was carbon dioxide. The contribution of nitrous oxide to mass 30 gave nitric oxide by difference. All of the contributions to mass

Table VIII

Mass Spectrometric Gas Analysis Data
for Thermal Decomposition of
3-Nitroso-5,5-diphenyl-2-oxazolidone at 185°

Sample 1 with CO₂

m/e mass	Background units	Sample Peak Height units	Corrected Peak Height units
14 ⁺	----	23.5	23.5
16 ⁺	----	31.6	31.6
18 ⁺	----	28.7	28.7
22 ⁺	----	3.5	3.5
28 ⁺	59.1	344.	285.
30 ⁺	----	69.1	69.1
44 ⁺	2.3	573.	571.

Sample 2 without CO₂

14 ⁺	1.1	49.0	47.9
18 ⁺	1.1	3.5	2.4
28 ⁺	51.2	519.	468.
30 ⁺	----	176.	176.
44 ⁺	3.4	364.	361.

Sample 3 with CO₂

12 ⁺	----	40.9	40.9
14 ⁺	----	31.6	31.6
18 ⁺	----	65.2	65.2
22 ⁺	----	5.0	5.0
28 ⁺	54.1	408.	354.
30 ⁺	----	118.	118.
44 ⁺	2.5	813.	810.

Sample 4 without CO₂

14 ⁺	2.7	48.3	45.6
18 ⁺	2.9	4.6	1.7
28 ⁺	54.4	529.	475.
30 ⁺	0.6	178.	177.
44 ⁺	10.7	384.	373.

28^1 were calculated, summed, and subtracted from the total peak height at mass 28. Thus nitrogen was obtained by difference. Calculation of the carbon dioxide contribution to mass 12 eliminated carbon monoxide as a possible constituent.

The mole fractions of the gases are tabulated below:

	<u>Runs 1 and 2</u>	<u>Runs 3 and 4</u>	<u>Average</u>	<u>moles of gas per mole of Nitroso compound</u>
CO ₂	0.433	0.426	0.430	0.879
N ₂	0.169	0.169	0.169	0.346
N ₂ O	0.255	0.262	0.258	0.529
NO	0.023	0.023	0.023	0.049
H ₂ O	0.120	0.120	0.120	0.247
Total				2.050

2. Decomposition of 3-nitroso-5,5-diphenyl-2-oxazolidone in the Absence of a Solvent at 120°

The solid nitroso compound (3.09 g., 0.0115 mole) was decomposed as previously except that the bath temperature was maintained at 120° until gas evolution had ceased, (usually twelve to thirteen hours).

The analytical procedures were identical. The parent 5,5-diphenyl-2-oxazolidone (1.54 g., 54%) was obtained directly from the reaction mixture after crystallization from ethanol-petroleum ether (55-70°).

The filtrate yielded 0.93 g., of a pale yellow oil E. A portion of oil E (0.180 g.) yielded 0.0412 g. (5.1%) of benzophenone-2,4-dinitrophenylhydrazone and when the filtrate from this derivative

1. For example, c.f. RELATIVE PEAK INTENSITIES.

was hydrated, desoxybenzoin-2,4-dinitrophenylhydrazone (0.130 g., 15.5%) was obtained.

The remaining oil E (0.750 g.) was chromatographed and re-chromatographed to yield a tar (0.051 g.), additional oxazolidone (0.070 g., 2.6%), benzophenone 2,4-dinitrophenylhydrazone (0.171 g., 5.0%), and hydrocarbon oil F (0.511 g.).

This hydrocarbon oil F was submitted to multicomponent ultra-violet spectrophotometric analysis as previously described. From this analysis, it was calculated that 0.321 g. (15.7%) of diphenylacetylene and 0.312 g. (15.1%) of 1,1-diphenylethylene were present in the reaction mixture.

The dry gas collected, (331 ml. S.T.P.), was more than theory, (259 ml.); this was 1.28 moles/mole of nitroso compound.

Quantitative Gas Analysis:

The analysis was run as previously with the exception that heating was maintained for fourteen hours. New sensitivities had to be run since the sensitivity of the mass spectrometer changes with time; however, the cracking patterns remained the same. A tabulation of the cracking patterns and the new sensitivities follows:

RELATIVE PEAK INTENSITIES

m/e mass	CO ₂	N ₂ O	NO	N ₂	H ₂ O
44 ⁺	1.00	1.00	-----	-----	-----
30 ⁺	-----	0.329	1.00	-----	-----
28 ⁺	0.0736	0.177	0.0863	1.00	-----
22 ⁺	0.0101	-----	-----	-----	-----
18 ⁺	-----	-----	-----	-----	1.00
14 ⁺	-----	0.0562	0.0441	0.0560	-----
12 ⁺	0.0729	-----	-----	-----	-----
k($\frac{div}{mm}$)	16.8	12.0	20.6	19.8	6.52

Table IX

Mass Spectrometric Gas Analysis Data
for Thermal Decomposition of
3-Nitroso-5,5-diphenyl-2-oxazolidone at 120°

Sample 5 with CO₂

m/e mass	Background units	Sample Peak Height units	Corrected Peak Height units
12 ⁺	----	32.5	32.5
14 ⁺	----	63.3	63.3
16 ⁺	2.2	60.1	57.9
18 ⁺	0.6	17.6	17.0
22 ⁺	----	4.7	4.7
28 ⁺	42.2	518.	476.
30 ⁺	----	111.	111.
44 ⁺	16.0	662.	646.

Sample 6 without CO₂

12 ⁺	3.8	2.6	----
14 ⁺	5.3	71.6	66.3
16 ⁺	6.8	18.2	11.4
18 ⁺	6.2	4.7	----
28 ⁺	62.1	508.	446.
30 ⁺	3.8	138.	134.
44 ⁺	56.3	294.	238.

Sample 7 with CO₂

12 ⁺	0.6	28.0	27.4
14 ⁺	4.5	51.9	47.4
16 ⁺	4.0	52.0	48.0
18 ⁺	0.6	29.5	28.9
22 ⁺	----	4.1	4.1
28 ⁺	57.3	443.	386.
30 ⁺	----	81.5	81.5
44 ⁺	27.5	555.	528.

Sample 8 without CO₂

12 ⁺	3.3	4.1	0.8
14 ⁺	6.0	73.8	67.8
16 ⁺	7.3	19.1	11.8
18 ⁺	6.5	6.2	----
28 ⁺	69.1	537.	468.
30 ⁺	5.9	131.	125.
44 ⁺	65.7	304.	238.

The calculations are exactly the same as the previous case:

The mole fractions of the gases are tabulated below:

	<u>Runs 5 and 6</u>	<u>Runs 7 and 8</u>	<u>Average</u>	<u>moles of gas per mole of Nitroso compound</u>
CO ₂	0.391	0.387	0.389	0.528
N ₂	0.298	0.288	0.293	0.398
N ₂ O	0.239	0.222	0.230	0.313
NO	0.034	0.026	0.030	0.041
H ₂ O	<u>0.038</u>	<u>0.077</u>	<u>0.058</u>	<u>0.080</u>
Total				1.360

3. Decomposition of 3-Nitroso-5,5-diphenyl-2-oxazolidone at 153 and 168° in Various Solvents

A typical reaction is described: A 25 x 200 mm. test tube, provided with an air condenser, was placed in the center hole of a three liter, three-necked flask containing refluxing cumene or t-butylbenzene. The nitroso compound and a solvent were placed in the test tube. After two hours the test tube was removed and cooled. The crystals which separated were 5,5-diphenyl-2-oxazolidone. The filtrate was carefully concentrated. The recovered solvent was checked by refractive index and infrared spectrum and was found to be identical with the starting solvent. A part of the remaining oil, which usually contained a small amount of solvent, was treated with freshly prepared 2,4-dinitrophenylhydrazine reagent. When the carbonyl derivative had crystallized, the filtrate was, in some cases, refluxed with mercuric sulfate and sulfuric acid in order to hydrate the diphenylacetylene present and recover it as desoxybenzoin

2,4-dinitrophenylhydrazones. In some cases, the solvent was adsorbed on alumina strongly enough so that the diphenylacetylene and 1,1-diphenylethylene mixture could be selectively removed. In these cases, the hydrocarbon mixture was submitted to multicomponent ultraviolet spectrophotometric analysis. The results are found in Table X.

4. Decomposition of 3-Nitroso-5,5-diphenyl-2-oxazolidone Under Various Conditions:

a. In Cumene and In the Presence of Air at 153°

The nitroso compound (4.08 g., 0.0152 mole) and cumene (52.0 g.) were placed in a previously dried 250 ml. flask. This flask was connected through a condenser to a dry-ice trap. The flask was heated at reflux temperature (153°) for two hours and then cooled overnight. Filtration yielded 5,5-diphenyl-2-oxazolidone, (2.69 g., 74.1%), and 59 ml. of solution G.

Some of the solution G (44 ml.), was carefully concentrated to a viscous oil H. The small forerun, (0.68 g.), was treated with freshly prepared 3,5-dinitrobenzoyl chloride¹ to yield the methyl derivative, (0.0330 g., 1.3%), m.p. 107.7-108.2°.¹

Viscous oil H was chromatographed on a 5.5 x 19 cm. column packed with alumina and developed with 2% ethanol in benzene. Four cuts were obtained. The first was largely cumene; the second, was largely acetophenone; the third, was more parent oxazolidone, (0.129 g. 4.4%); and the fourth, was an unidentified tar, (0.353 g.).

Some of cumene solution G (5 ml.), was treated with freshly

1. N. D. Cheronis and J. B. Entriken, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 221, also gives melting point of methyl derivative, (108°), p. 370.

Table X
Products of the Decomposition of 3-Nitroso-5,5-diphenyl-2-oxazolidone, IV,
in Various Solvents

Run	Temp.	Solvent	g. Solvent used	g. Solvent recovered	g. IV used	% Yield Of Products: oxazolidone; $\phi_2\text{CO}^a$; $\phi\text{C}=\phi^b$; $\phi\text{C}=\phi^c$; $\phi_2\text{C}-\text{CH}_2^c$
1	153	None	None	None	4.66	50.6 5.4 17.9 20.1 21.2
2	153	t-Bu ϕ	16.07	14.89	4.91	52.2 5.3 18.3
3	153	ϕNO_2	22.41	20.99	4.18	48.9 5.6 17.5 20.0 21.5
4	153	p-xylene	0.541	None	3.91	52.0 5.9
5	153	p-xylene	24.22	23.68	4.04	80.1 (18.4% p-toluic acid only) ^d
6	153	$\phi\text{CO}_2\text{Me}$	17.83	17.06	3.81	54.1 5.7 17.9
7	153	$\text{Cl}_3\text{CCl}-\text{CCl}_2$	38.71	27.63	3.96	47.8 ^e
8	153	ϕBr	26.17	25.06	4.39	52.8 5.7 18.3 19.8 21.0
9	153	Naphthalene	15.21	14.68	4.20	48.0 5.8 18.0
10	153	$(\text{CH}_2\text{OH})_2$	17.31	17.02	3.57	51.2 5.6
11	153	cumene	24.71	23.99	4.14	19.7 (22.1% ϕCOMe only) ^f
12	168	None	None	None	5.19	39.6 5.6 22.9 26.3
13	168	t-Bu ϕ	18.31	17.33	4.69	41.9 5.7 21.1

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Note: blank spaces in table indicate that no analysis was run.

a. As benzophenone 2,4-dinitrophenylhydrazone.

b. As desoxybenzoil 2,4-dinitrophenylhydrazone.

c. Determined by multicomponent ultraviolet spectrophotometric analysis:

Run	1	3	8	12
optical density at 2500A	0.672	0.536	0.770	0.674
optical density at 2700A	0.710	0.562	0.815	0.693
g./100 ml. $\phi\text{C}=\phi$ ($\times 10^{-4}$)	4.48	3.54	5.14	4.27
g./100 ml. $\phi_2\text{C}-\text{CH}_2$ ($\times 10^{-4}$)	4.80	3.85	5.50	4.98
g. in hydrocarbon fraction	1.285	1.160	1.197	1.760

d. p-toluic acid, m.p. 179.4-180.0°, showing no depression when mixed with an authentic sample (% yield based on moles of nitroso compound).

e. A large amount of tar formed (solvent formed tar under identical conditions).

f. As acetophenone 2,4-dinitrophenylhydrazone (based on moles of nitroso compound).

prepared 2,4-dinitrophenylhydrazine reagent. After warming slightly, this was allowed to cool overnight. The precipitate was collected and dried at 120°. (The filtrate when refluxed with mercuric sulfate and sulfuric acid and cooled, yielded no precipitate.) The solid was chromatographed on a column packed with alumina and developed with benzene. An orange solid, (0.169 g.), m.p. 227-249°, was obtained. This solid, (0.0025 g.), was dissolved in petroleum ether-chloroform¹ and chromatographed on a column packed with silicic acid and developed with 10% ether in Skellysolve B.¹ Two zones appeared after the passage of 20 ml. of developer. The lower, orange zone, was much larger, than the upper, yellow zone. The lower zone was acetophenone 2,4-dinitrophenylhydrazone, (0.165 g., 42.7% based on nitroso compound), m.p. 249-250°, and the upper zone was acetone 2,4-dinitrophenylhydrazone, (0.0033 g., 1.1% based on nitroso compound), m.p. 127.9-128.6°. ²

b. In Cumene and in a Nitrogen Atmosphere at 153°

Oxygen-free, water-free nitrogen was prepared as follows: oil-pumped nitrogen³ was passed into an absorption train such as the one described by Fieser.⁴ This was modified by the use of cumene as the solvent for the metal ketil which was prepared from benzophenone and

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1. Skellysolve B is petroleum ether, boiling range, 55-70°.
 2. E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 374, gives melting point as 128°.
 3. Oil-pumped nitrogen used from cylinders supplied by Linde Air Products.
 4. L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., Boston, Mass., 3rd Edition, 1955, p. 299.

sodium-potassium alloy. The purified nitrogen was then passed into a 500 ml. trap and then into the reaction flask.

The solid nitroso compound, (4.35 g., 0.0163 mole), and cumene, (53.5 g.), were placed in a previously dried 250 ml. flask. Purified nitrogen was passed into the system for four hours before the reaction flask was heated. The nitrogen flow was continued until after the reaction was completed.

The products were 5,5-diphenyl-2-oxazolidone, (78.9%), acetophenone, (29.8%, based on nitroso compound), acetone, (1%, based on nitroso compound), and methanol, (1%, based on nitroso compound).

When nitric oxide was passed into cumene in the reaction flask using the procedure described above, the products were acetophenone, acetone, and methanol. No cumene dimer, phenol, formaldehyde, or nitro compounds were found.

c. With Added 2,3-Dimethyl-2,3-diphenylbutane in the Presence of Air at 153°

The solid nitroso compound, (4.61 g., 0.0172 mole), cumene, (49.70 g.), and 2,3-dimethyl-2,3-diphenylbutane,¹ (0.104 g.), were placed in a previously dried 250 ml. flask. The reaction was run as previously; the products were also determined in an analogous manner except for the recovery of 2,3-dimethyl-2,3-diphenylbutane. When the oil from the reaction mixture was chromatographed, the first fraction yielded, in addition to cumene, 2,3-dimethyl-2,3-diphenylbutane, (0.0943 g., 90.7% recovery). The other products of the reac-

1. M. S. Kharasch, H. C. McBay, and W. H. Urry, J. Org. Chem., 10, 401 (1945).

tion were 5,5-diphenyl-2-oxazolidone, (83.6%), acetophenone, (41.1%, based on nitroso compound), acetone, (1.6%, based on nitroso compound), and methanol, (1.1%, based on nitroso compound).

d. With Added α -Methylstyrene in the Presence of Air at 100°

The nitroso compound, (0.692 g.), was heated in a 100 ml. flask with 50 ml. of freshly distilled α -methylstyrene for twenty-four hours at 100°. A blank experiment was run in the same manner.

After cooling, the α -methylstyrene was distilled from the blank to leave a solid polymer, (7.70 g.). The sample containing the nitroso compound, was filtered to yield the parent oxazolidone, (0.183 g.). The filtrate was carefully concentrated to yield an oil J (3.62 g.). A portion of oil J (1.47 g.), was treated with freshly prepared 2,4-dinitrophenylhydrazine reagent, and, after working up in the usual manner, the derivative of acetophenone was obtained, (0.131 g., 41.7% based on nitroso compound). The remaining oil J (2.15 g.), was chromatographed on a column packed with alumina and developed with benzene. Four fractions were obtained: the first was α -methylstyrene, the second was acetophenone, the third was parent oxazolidone, (0.198 g.), and the last was a tar, (1.70 g.). This tar had no carbonyl band in its infrared spectrum. The results of this experiment are:

Product	Yield
parent oxazolidone	84%
acetophenone	42%
tar	2.86 g.
tar (blank)	7.70 g.

e. With Added 1,1-Diphenylethylene in the Presence of Air at 185°

The nitroso compound, (2.78 g., 0.0104 mole), and 1,1-diphenylethylene, (5.42 g., 0.0301 mole), were heated at 185° until the evolution of gas was complete, (forty minutes). The reaction mixture was cooled and diluted to 25 ml. with ethanol. An aliquot (1/5) was treated with freshly prepared 2,4-dinitrophenylhydrazine solution. The derivative of benzophenone, (0.0764 g., 10.1% based on nitroso compound), was obtained after working up in the usual manner. The filtrate from which the crude derivative separated, was refluxed with mercuric sulfate, (2 g.) and sulfuric acid, (5 ml.), and then cooled. No derivative was obtained.

The remaining ethanol solution was concentrated and chromatographed on a column packed with alumina and developed with benzene. The first cut was 1,1-diphenylethylene, the second cut was benzophenone, the third cut yielded 5,5-diphenyl-2-oxazolidone, (1.72 g., 87%), and the fourth and most strongly adsorbed cut yielded a small amount of tar.

5. The Stability of 5,5-Diphenyl-2-oxazolidone to Heat

The oxazolidone, (7.47 g.), was heated at 220-225° for twenty-six hours in a previously dried 100 ml. flask connected to a gas collecting device. After cooling, 15 ml. of petroleum ether (30-60°) and 3 ml. of ethanol were added. Filtration yielded the starting material, (7.23 g., 97%), m.p. 200-201°. The filtrate was concentrated and yielded additional product, (0.14 g.), m.p. 195-199°.

No gas evolution was observed.

B. 3-Nitroso-5-methyl-5-phenyl-2-oxazolidone, V 1. Decomposition in the Absence of a Solvent at 185°

The solid nitroso compound V, (22.10 g., 0.107 mole), was placed in a previously dried 100 ml. flask connected to a gas collecting device. The flask was heated slowly in a salt bath until a temperature of 185-190° had been reached and maintained at that temperature until the evolution of gas had ceased, (usually thirty to forty minutes). The decomposition was active but never violent.

After cooling, the brown-mushy solid was mixed with four portions of petroleum ether (30-60°), decanting the solvent after each mixing. The combined petroleum ether fraction was concentrated to red-brown oil K (6.67 g.).

The solid, (8.75 g.), was dissolved in 15 ml. of hot toluene and cooled in a dry-ice bath. The solid obtained was 5-methyl-5-phenyl-2-oxazolidone, (7.16 g., 37.7%), m.p. 146-147°. ¹ The filtrate was chromatographed on a column packed with alumina and developed with benzene. Additional oxazolidone, (0.11 g., 0.6%), and a dark brown gum, (1.49 g.), were obtained. The gum could not be identified. The infrared spectrum showed that carbonyl and nitrogen-hydrogen bands were absent.

A sample of oil K (0.46 g.) was treated with freshly prepared

1. M. S. Newman and A. Kutner, J. Am. Chem. Soc., 73, 4199 (1951), give the melting point 146.2-147.2°.

2,4-dinitrophenylhydrazine reagent. The precipitate after workup yielded the acetophenone derivative, (0.180 g., 8.1%), m.p. 248-249°.¹ The filtrate, containing oil K and unreacted reagent, was refluxed with mercuric sulfate, (2 g.) and sulfuric acid (5 ml.) and then cooled. Workup in the usual manner (by chromatography) yielded two zones, weakly adsorbed propiophenone 2,4-dinitrophenylhydrazone, (0.171 g., 7.4%), m.p. 190-191°,² and strongly adsorbed 1-phenylpropan-1,2-dione 2,4-dinitrophenylosazone, (0.282 g., 7.5%), m.p. 263-264°.³

Anal: Calcd. for $C_{21}H_{16}N_8O_8$: C, 49.6; H, 3.2; N, 22.0

Found: C, 49.4; H, 3.1; N, 21.9

Another sample of oil K (1.54 g.), was chromatographed on a column packed with silicic acid and developed with Skellysolve B, to yield four fractions. The first fraction L (0.521 g.), was all hydrocarbons. The second fraction, treated with freshly prepared 2,4-dinitrophenylhydrazine reagent, yielded the acetophenone derivative, (0.579 g., 7.8%), m.p. 248-249°. The third fraction was more of the oxazolidone, (0.525 g., 12.8%), m.p. 146-147°. An unidentified tar, (0.211 g.), remained on the column.

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1. E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 388, give melting point 249-250°.
 2. Ibid., p. 390, give melting point 190-191°.
 3. 1-Phenylpropan-1,2-dione prepared according to J. Wegmann and H. Dann, *Helv. Chim. Acta.*, 29, 1248 (1946), and the osazone prepared by treating the diketone with freshly prepared 2,4-dinitrophenylhydrazine reagent.

Part of L, the hydrocarbon fraction,¹ (0.403 g.), was ozonized and worked up as previously described. From the neutral portion of the ozonolysis products was made acetophenone 2,4-dinitrophenylhydrazones, (0.606 g., 10.5%), m.p. 248-249°.

The gas collected, (2615 ml., S.T.P.), was more than theory, (2410 ml.); this was 1.09 moles gas/mole of nitroso compound.

Sources of 1-Phenylpropan-1,2-dione 2,4-Dinitrophenyl-osazone, XLVIII.

From Phenylacetone

Phenylacetone, (0.668 g., 0.050 mole), was refluxed two hours with 2,4-dinitrophenylhydrazine, (1.98 g., 0.100 mole), mercuric sulfate, (1.48 g., 0.050 mole), sulfuric acid, (20 ml.), water, (15 ml.), and ethanol, (100 ml.). After cooling, the solid was triturated with boiling ethyl acetate to remove mercury salts, and an aliquot of the filtrate chromatographed on a column packed with alumina. Development with benzene yielded the osazone XLVIII (2.27 g., 89%), m.p. 264-265°.

From Propiophenone

Propiophenone, (0.633 g., 0.0472 mole), was refluxed two hours with 2,4-dinitrophenylhydrazine, (1.91 g., 0.0965 mole), mercuric sulfate, (1.41 g., 0.0474 mole), sulfuric acid, (20 ml.), water, (15 ml.), and ethanol, (100 ml.). After cooling, the solid was triturated with boiling ethyl acetate to remove mercury salts, and an aliquot of the filtrate chromatographed on a column packed with

1. A sample of this hydrocarbon fraction, treated with freshly prepared, 2,4-dinitrophenylhydrazine reagent, yielded no derivative prior to ozonolysis.

alumina. Development with benzene yielded first propiophenone 2,4-dinitrophenylhydrazone, (1.21 g., 81%), m.p. 190-191°, and the osazone XLVIII, (0.29 g., 12%), m.p. 264-265°.

From 1-Phenyl-1-propyne

Phenylmethylacetylene or 1-phenyl-1-propyne,¹ (0.436 g., 0.0376 mole), was refluxed two hours with 2,4-dinitrophenylhydrazine, (1.12 g., 0.0377 mole) mercuric sulfate, (1.61 g., 0.0544 mole), sulfuric acid, (20 ml.), water (15 ml.), and ethanol, (100 ml.). After cooling, the solid was triturated with boiling ethyl acetate to remove mercury salts, and an aliquot of the filtrate chromatographed on a column packed with alumina. Development with benzene yielded first propiophenone 2,4-dinitrophenylhydrazone, (0.871 g., 74%), m.p. 190-191°, and the osazone XLVIII, (0.206 g., 11%), m.p. 263-265°.

2. Decomposition of 3-Nitroso-5-methyl-5-phenyl-2-oxazolidone in Various Solvents at 153°

A typical reaction is described: A 25 x 200 mm. test tube, provided with an air condenser, was placed in the center hole of a three liter, three-necked flask containing refluxing cumene. The nitroso compound and a solvent were placed in the test tube. After two hours, the test tube was removed and cooled. Crystalline 5-methyl-5-phenyl-2-oxazolidone separated. An aliquot of the filtrate was treated with freshly prepared 2,4-dinitrophenylhydrazine reagent. When this carbonyl derivative crystallized, the filtrate was refluxed with mercuric sulfate and sulfuric acid and the products recovered in

1. Phenylmethylacetylene is synonymous with 1-phenyl-1-propyne. This compound was made according to the method of K. N. Campbell and M. J. O'Conner, J. Am. Chem. Soc., 61, 2897 (1939).

the usual manner.

The remaining reaction mixture was concentrated. The recovered solvent, checked by refractive index and infrared spectrum, was identical with the starting solvent. The concentrate was chromatographed on a column packed with alumina and developed with benzene. Additional parent oxazolidone was recovered. The results are found in Table XI.

C. 3-Nitroso-1-oxa-3-azaspiro[4.5]decan-2-one, VI

1. Decomposition in the Absence of a Solvent at 185°

The solid nitroso compound, VI,¹ (8.20 g., 0.0446 mole), was placed in a previously dried 100 ml. flask connected to a gas collecting device. The flask was heated slowly in a salt bath until a temperature of 185-190° had been reached and maintained at that temperature until the evolution of gas had ceased, (usually thirty to forty minutes.). The decomposition was moderate initially but became violent.

After cooling, the brown-black tarry mass was dissolved in 10 ml. of chloroform. One-half of this solution M was treated with freshly prepared 2,4-dinitrophenylhydrazine reagent but no derivative was obtained.

The remaining chloroform solution M was chromatographed on a column packed with alumina and developed with 10% ether in Skelly-

1. M. S. Newman, J. Am. Chem. Soc. 71, 378 (1949).

Table XI

Products of the Decomposition of 3-Nitroso-5-methyl-5-phenyl-2-oxazolidone,
V, in Various Solvents at 153°

Run	Temp.	Solvent	g. Solvent Used	g. Solvent Recovered	g. V Used	% Yield of Products: oxazolidone; ϕ COMe; ^a ϕ CMe; ^b osazone ^c			
14	153	None	None	None	4.67	63.6	7.1	6.5	5.7
15	153	ϕ NO ₂	23.19	22.01	4.26	61.4	7.3	7.0	6.4
16	153	Cumene	24.11	22.93	4.63	87.7	28.2 ^d	none	none

Note: α -methylstyrene was shown to be present in each case by its infrared spectrum.

- As acetophenone 2,4-dinitrophenylhydrazone.
- As propiophenone 2,4-dinitrophenylhydrazone.
- As 1-phenylpropan-1,2-dione 2,4-dinitrophenylosazone.
- As acetophenone 2,4-dinitrophenylhydrazone (based on moles of nitroso compound).

solve B. The first fraction collected, concentrated and cooled, yielded 1-oxa-3-azaspiro[4.5]decan-2-one, (1.96 g., 56.8%), m.p. 101-102°.¹ The large amount of black, carbon-like tar remaining on the column could not be identified.

The gas collected, (963 ml., S.T.P.), was less than theory, (998 ml.); this was 0.965 moles of gas/mole of nitroso compound.

2. Decomposition of 3-Nitroso-1-oxa-3-azaspiro[4.5]decan-2-one at 153° in Various Solvents

A typical reaction is described: A 25 x 200 mm. test tube, provided with an air condenser, was placed in the center hole of a three liter, three-necked flask containing refluxing cumene. The nitroso compound and a solvent were placed in the test tube. After two hours, the test tube was removed and cooled.

An aliquot of this solution, treated with 2,4-dinitrophenylhydrazine reagent, yielded the cyclohexanone derivative, m.p. 161-162°.² (This derivative was not obtained in all cases).

The remaining reaction mixture was concentrated. The recovered solvent, checked by refractive index and infrared spectrum, was identical to the starting solvent.

The oxazolidone was recovered by chromatography, using the procedure described in the preceding section. The results are found in Table XII.

1. M. S. Newman, J. Am. Chem. Soc. 71, 378 (1949), reports melting point 101.0-102.4°.
2. R. L. Shriner, and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 262, report melting point 162°.

Table XII

Products of the Decomposition of 3-Nitroso-1-oxa-3-azaspiro[4.5]decan-2-one,
VI, in Various Solvents at 153°

Run	Temp.	Solvent	g. Solvent Used	g. Solvent Recovered	g. VI Used	%Yield of Products: oxazolidone; cyclohexanone ^a	
17	153	None	None	None	3.61	70.2	None
18	153	Ø NO ₂	26.12	26.01	3.41	65.3	2.1
19	153	Ø CO ₂ Me	24.77	23.91	3.77	66.5	1.4
20	153	Cumene	21.62	20.95	4.01	89.6	(41.1% acetophenone only) ^b

a. As cyclohexanone 2,4-dinitrophenylhydrazone.

b. As acetophenone 2,4-dinitrophenylhydrazone (yield based on nitroso compound).

D. 3-Nitrosospiro[fluorene-9',5-oxazolidin]-2-one, VII

VII

1. Spiro[fluorene-9',5-oxazolidin]-2-one

A typical Reformatsky reaction¹ is described: In a 500 ml. three-necked, round-bottomed flask, equipped with Hershberg stirrer and take-off condenser, was charged fluorenone, (18.0 g., 0.1 mole), dry, thiophene-free benzene, (105 ml.), and freshly sanded zinc foil, (14.1 g., 0.217 mole). Some benzene-water azeotrope, 10 ml., was distilled, and while still refluxing, methyl α -bromoacetate, (21.1 g., 0.138 mole), was added dropwise over a thirty minute period. Reaction was sluggish. When the ester addition was completed, the reaction mixture was refluxed an additional thirty minutes, cooled, and poured into a slight excess of cold, dilute hydrochloric acid. The zinc recovered amounted to 5.6 g., (zinc used: 8.5 g., 0.131 mole).

The aqueous phase was washed several times with ether-benzene and the organic phases combined. The combined organic layer was washed in turn with water, sodium bicarbonate, and saturated sodium chloride solution until all of the alkali was removed. The solvent was removed at 40° under reduced pressure (1 mm. Hg) since at 60-80° dehydration occurred. The oil N obtained could not be crystallized.

1. For a thorough discussion of this reaction see, R. L. Shriner in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 1-37.

This oil did not decolorize 2% potassium permanganate. The infrared spectrum indicated a hydroxyl band. $2.92\mu(s)$.

The oil N was treated with anhydrous hydrazine (7.5 g., 0.234 mole), in methanol (100 ml.). The solution was warmed slightly and allowed to stand overnight. The methanol and excess hydrazine were removed at 40° under reduced pressure (1 mm. Hg) and placed in a vacuum desiccator over sulfuric acid. The resulting oil P could not be crystallized.

A solution of oil P in 2N hydrochloric acid, (60 ml.), was placed in a 500 ml. three-necked, round-bottomed flask equipped with Hershberg stirrer, thermometer, and dropping funnel. Sodium nitrite (6.9 g., 0.10 mole) in water (30 ml.) was added with stirring at $10-12^{\circ}$. After this addition, urea (1.5 g.) was added to destroy the excess nitrite. Skellysolve B (50 ml.) was added and the reaction mixture was warmed to 50° . A vigorous evolution of nitrogen took place during a twenty-minute period. After cooling, tan crystals, m.p. $220-223^{\circ}$, formed. After two recrystallizations from ethanol, a colorless product, m.p. $230.8-231.3^{\circ}$, was obtained. The overall yield from fluorenone was 12.1 g., 51%.

Anal.: Calcd. for $C_{15}H_{11}NO_2$: C, 75.9; H, 4.7; N, 5.9.

Found: C, 76.1; H, 4.7; N, 6.0.

2. Nitrosation of the Oxazolidone

A solution of nitrosyl chloride (7.5 g., 0.114 mole) in acetic anhydride (40 ml.) was added dropwise with stirring to a suspension of oxazolidone, (23.7 g., 0.100 mole), in dry pyridine, (150 ml.),

maintaining the temperature at 0-5°. After the addition period of thirty minutes, the slurry was poured into iced water, (250 g.). The yellow precipitate was collected and dried in vacuo. Recrystallization from benzene-Skellysolve B yielded yellow needles, (23.9 g., 90%), m.p. 165° dec.

Anal: Calcd. for $C_{15}H_{10}N_2O_3$: C, 67.7; H, 3.8; N, 10.5.

Found: C, 67.6; H, 4.0; N, 10.4.

3. Alkaline Decomposition of the Nitroso Compound, VII.

To a 250 ml. flask, connected to a gas collecting device and containing nitroso compound VII, (10.42 g., 0.0392 mole), and methanol (120 ml.), was added dropwise¹ 50% potassium hydroxide until there was no further evolution of nitrogen.² The reaction mixture was maintained at 0° since at higher temperatures the reaction was violent. The red-violet reaction mixture, diluted with water (500 ml.) was washed with several portions of benzene. The benzene washes were combined, concentrated in the dark³ at 40° under vacuum, (25 mm. Hg), and chromatographed on a column packed with alumina and developed with benzene. The main, pale yellow fraction was concentrated to 50 ml. in the dark at 40° under vacuum, (25 mm. Hg), and treated with Skellysolve B (10 ml.). The precipitate, m.p. 93-98.5° was twice recrystallized from methanol to yield

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1. A trace of base produced a reaction which went to completion only after a long time.
 2. Evolution of nitrogen was quantitative (1 mole gas/mole nitroso compound).
 3. The product was light-sensitive.

9-(methoxymethylene)fluorene,¹ (7.11 g., 87%), m.p. 103.8-104.3°.

Anal.: Calcd. for $C_{15}H_{12}O$: C, 86.5; H, 5.8

Found: C, 86.4; H, 5.8

The picrate² of 9-(methoxymethylene)fluorene was prepared. Recrystallization from ethanol yielded orange needles of the picrate, m.p. 194.8-195.7°.

Anal.: Calcd. for $C_{21}H_{15}N_3O_8$: C, 57.7; H, 3.5; N, 9.6

Found: C, 57.7; H, 3.7; N, 9.6

A very small violet band was removed from the extruded column with boiling ethanol. The ethanol solution was concentrated to solid. Recrystallization from nitrobenzene yielded a metallic-violet solid, (0.0264 g.), m.p. 301-302°, which was not identified. The analysis agrees with the empirical formula $C_{28}H_{19}NO_2$.

Anal.: Calcd. for $C_{28}H_{19}NO_2$: C, 83.8; H, 4.8; N, 3.5

Found: C, 83.7; H, 4.9; N, 3.5

E. Unsuccessful Attempts to Obtain α -hydroxyesters by the Reformatsky Reaction

1. Methyl 1-hydroxyhydrinaneacetate³

To a flask, containing α -hydrindone (37.6 g., 0.285 mole), dry, thiophene-free benzene, (100 ml.), and freshly sanded zinc foil

1. A sample for comparison was prepared according to the method of W. G. Brown and B. A. Bluestein, J. Am. Chem. Soc. 65, 1082 (1943). The reported melting point is 104°. The compound is light sensitive.
2. Picrate prepared by method of R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p.180.
3. J. von Braun, E. Dansiger, and Z. Koehler, Ber. 50, 57 (1917) tried to make the ethyl ester but it dehydrated when distilled.

(38.0 g., 0.585 mole), was added dropwise methyl α -bromoacetate, (59.0 g., 0.386 mole). A vigorous reaction took place and external cooling was necessary. When the addition of the ester was complete, the mixture was refluxed for an additional thirty minutes. The reaction mixture was cooled, poured into a slight excess of cold dilute hydrochloric acid, and worked up in the usual manner. The zinc recovered amounted to 13.2 g. (zinc used, 24.8 g., 0.382 mole). After a small forerun in which hydrindone could be detected, a product, (42.1 g., 71.9%), b.p. 139-141°/1 mm. with decomposition, was collected. The infrared spectrum indicated hydroxyl and unsaturation bands. The product reacted slowly with 2% aqueous potassium permanganate solution.

When a similar reaction mixture was distilled in a modified Hickman still, the product also reacted slowly with 2% aqueous potassium permanganate.

2. Methyl 1-hydroxytetralinacetate¹

To a flask, containing 14.6 g. (0.1 mole) of α -tetralone, (14.6 g., 0.1 mole), dry, thiophene-free benzene (50 ml.) and freshly sanded zinc foil, (13.0 g., 0.2 mole) was added dropwise methyl α -bromoacetate, (20.3 g., 0.133 mole). A vigorous reaction took place and external cooling was necessary. When the addition of the ester was complete, the mixture was refluxed for an additional thirty minutes. The reaction mixture was cooled, poured into a slight excess of cold dilute hydrochloric acid, and worked up in the usual manner. The zinc recovered amounted to 4.6 g. (zinc used, 8.4 g.,

1. G. Schroeter, Ber. 58, 713 (1925) prepared the ethyl ester in poor yield since the main fraction dehydrated.

0.129 mole). After a small forerun in which α -tetralone could be detected, a product, (15.5 g., 66.0%), b.p. 125-127°/0.2 mm. Hg with decomposition, was collected. The infrared spectrum indicated very little hydroxyl band and a large unsaturation band. The product reacted rapidly with 2% aqueous potassium permanganate solution.

Other similar reaction mixtures yielded the unsaturated ester.

SUMMARY

The thermal decomposition of a series of three di-5-substituted 3-nitroso-2-oxazolidones has been investigated, the results described, and a mechanism proposed. The main product in all cases was the parent oxazolidone.

When at least one of the substituents was phenyl, the by-products were 1,1-disubstituted ethylenes, ketones, and disubstituted acetylenes. The ketones were the result of oxidative cleavage of the ethylenic bond by nitric oxide. The acetylenes, which had the same number of carbons as the ethylenes, were the result of a rearrangement presumably involving the migration of a phenyl group.

The dialkylated compound yielded a small amount of ketone and tar as the only by-products.

The effect of temperature on the amounts of decomposition products of the diphenyl substituted compound was studied. In addition, a quantitative analysis of the gases of decomposition was made for this compound.

The effect of organic solvents on the mode of decomposition was studied for all of the compounds.

3-Nitrospiro[fluorene-9',5-oxazolidin]-2-one was prepared and decomposed with potassium hydroxide in methanol. 9-(Methoxymethylene) fluorene was the main product. This result substantiated the mechanism proposed by Newman and Kutner for the alkaline decomposition of 5-substituted 3-nitroso-2-oxazolidones.

AUTOBIOGRAPHY

I, Alan Edward Weinberg, was born in Cleveland, Ohio, December 11, 1927. I received my secondary school education in the public schools of Cleveland Heights, Ohio. My undergraduate training was obtained at The Case Institute Of Technology of Cleveland, Ohio, from which I received the degree Bachelor of Chemical Engineering in 1949. I was employed from 1949 to 1951 by Strong Cobb & Company, Cleveland, Ohio, as a research chemist. I have been attending the Ohio State University since 1952, where I specialized in the study of Organic Chemistry. While in residence at the Ohio State University, I served as a Graduate Assistant in General Chemistry during the year 1952-1953, as a Graduate Assistant in Organic Chemistry during the year 1953-1954, and as an Assistant Instructor in Organic Chemistry during the year 1954-1955. I received an appointment as a Carbide and Carbon Fellow in 1955. I held this latter position while completing the requirements for the degree of Doctor of Philosophy.