24% of the product had rearranged to deltacyclyl brosylate. Solvolysis of the brosylate was carried out immediately: ir (neat) 3039 (cyclopropyl C-H stretching), 2105 (C-D stretching), 1575 (aromatic C=C stretching), 1183 cm^{-1}; nmr (100 MHz, CCl_4) τ 8.3-8.9 (m, 2 H), 7.6-8.3 (m, 5 H), 7.2-7.6 (broad, 3 H, bridgehead protons), 5.96 (s, 1 H, -CHOBs).

Solvolysis of 5,5-Dideuterio-*exo*-7-isodeltacyclyl Brosylate Product Study. The solvolysis of 5,5-dideuterio-*exo*-7-isodeltacyclyl brosylate was accomplished following the same procedure as for isodeltacyclyl brosylate. Brosylate (43 mg, 0.12 mmol, 0.70 D) was added to 3.2 ml of 0.04 *M* NaOAc-HOAc solution and allowed to solvolyze at 40° for 48 hr. After work-up, two products were detected by vpc in the ratio of 3.3:96.7 (column 1, 155°, 66 ml/min, 17 min, 15 min). The minor product was not isolated, but had the same retention time as isodeltacyclyl acetate. Nmr analysis utilizing $Eu(fod)_3$ indicated that deuterium was scrambled between C-9 and C-5 exclusively, in the ratio of 1:1.8, respectively, correcting for the amount of brosylate which had undergone rearrangement prior to solvolysis. The sum of the deuterium content at the two positions was 0.86 ± 0.05 D.

Acknowledgment. The authors gratefully acknowledge the generous support of this work by the National Science Foundation.

Registry No. *exo*-**4b**, 43187-23-1; *exo*-**4b**-*5,5-d*$_2$, 43187-24-2; *exo*-**4c**, 43187-25-3; *exo*-**4c**-*5,5-d*$_2$, 43187-26-4; *exo*-**4f**, 43187-27-5; *exo*-**4f**-*5,5-d*$_2$, 43187-28-6; *cis*-**5a**, 3721-35-5; *trans*-**5a**, 3721-36-6; *cis*-**5b**, 16506-98-2; *trans*-**5b**, 16544-46-0; 5-*endo*-6-*endo*-**6a**, 43187-30-0; 5-*exo*-6-*endo*-**6a**, 43187-31-1; 5-*endo*-6-*endo*-**6b**, 43187-32-2; 5-*endo*-6-*exo*-**6b**, 43187-33-3; 5-*exo*-6-*endo*-**6b**, 43187-34-4; 5-*exo*-6-*endo*-**6c**, 43187-35-5; 5-*exo*-6-*endo*-**6d**, 43187-36-6; 5-*exo*-6-*endo*-**6e**, 43187-37-7; *endo*-**7a**, 43187-38-8; *exo*-**7a**, 43187-39-9; *exo*-**7b**, 43187-40-2; *exo*-**7c**, 43187-41-3; **10**, 13084-56-5; *exo*-**12a**, 43187-43-5; *exo*-**12b**, 41850-57-1; propiolic acid, 471-25-0; diazo ketone (X = Cl), 43187-45-7; diazo ketone (X = OAc), 43187-46-8; *exo*-7-acetoxyisodeltacyclan-5-one ethanedithiol ketal, 43187-47-9.

References and Notes

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Pathways in the Base-Catalyzed Decomposition of Cyclic *N*-Nitroso Carbamates[1]

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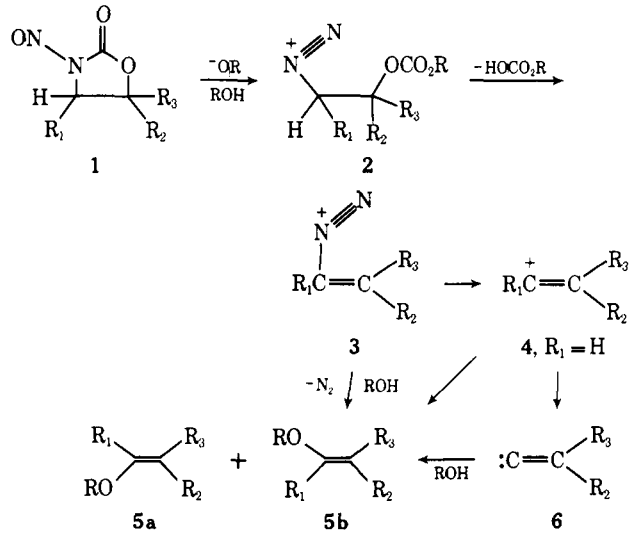
Received June 25, 1973

The scope and stereochemical aspects of the base-catalyzed decomposition of 3-nitroso-2-oxazolidones are examined. Though certain 3-nitroso-2-oxazolidones (**3**) when treated with base in alcohol produce vinyl ethers **5** in good yield, the reaction is not general. Vinyl ethers are obtained only when a vinyl diazonium ion **3** can be produced readily. This occurs if a proton at the 4 position of **1** can be readily lost from intermediate **2** and when the 5 position is substituted such that the carbonate of intermediate **2** becomes a good leaving group. If the 4 carbon is primary, then the 5 carbon must be tertiary or benzylic, whereas, if the 4 carbon is secondary, then the 5 carbon must be benzhydrylic for formation of a vinyl ether as the major product. If these conditions are not met, many different products, in particular carbonates and ketones, are formed presumably by loss of N_2 from **2** to afford an intermediate carbonium ion **24**. Thus, 3-nitroso-2-oxazolidones **9a-f** afford primarily products formally derived from **24** and even **9g** yields a significant amount of such compounds. However, **10b** gives only a trace of such derivatives, furnishing, instead, products derived from vinyl diazonium ion **3**.

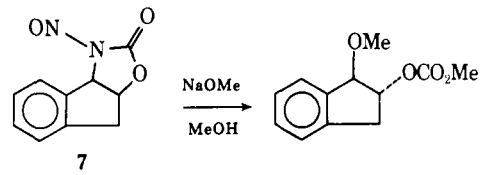
The base-catalyzed decomposition of *N*-nitroso carbamates is a well-known source of diazo and diazonium species.[2] Their cyclic analogs, the *N*-nitroso-2-oxazolidones contain an interesting feature. On base treatment, the original alcohol portion of the carbamate remains part of the same molecule that contains the diazo or diazotate group; hence neighboring group effects in these reactions can be evaluated. Earlier studies on the reaction of 3-nitroso-2-oxazolidones indicated that ketones, acetylenes, and vinyl ethers were among the products isolated.[3] Recent work by Newman and coworkers[4] has extended this reaction to a good yield synthesis of vinyl ethers **5** as a result of treatment of alcoholic solutions of certain 3-nitroso-2-oxazolidones (**1**) with base. The reaction was assumed to proceed by the elimination of monoalkyl carbonate and nitrogen from the diazonium intermediate **2**[5] to afford vinyl cation **4** which in alcohol is converted to **5** (Scheme I). When R_1 = H, evidence has been presented that an alkylidene carbene **6** is generated in aprotic media.[6]

Newman and coworkers have shown[6] that in the case of the *tert*-butyloxazolidone **1** (R_1 = H, R_2 = CH_3, R_3 = *tert*-butyl) there is a stereochemical preference leading mainly to the trans vinyl ether **5a** (or equivalent product of trapping cation **3** with a nucleophile). However, it has not been established whether stereochemistry is maintained in the conversion of stereoisomers of **1** into stereoisomeric **5**. Since our studies on INCO additions to olefins have provided a stereospecific entry into 4,5-disubstituted oxazolidones,[7] we decided to investigate the chemistry of such systems, *i.e.*, **1** (R_2 or R_3 = H), in order to relate the stereochemistry of the reactants and products.

Scheme I

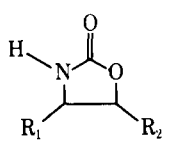


We were further tempted to investigate the scope of this reaction by preliminary results on the reaction of fused *N*-nitroso-2-oxazolidone **7** with methoxide.[8] The major product was not a vinyl ether but methyl (*trans*-1-methoxy)-2-indanyl carbonate (55%).

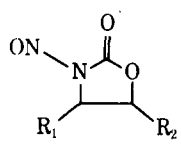


Results

The oxazolidones needed in this study were synthesized by several different methods. Thus, reaction of *trans*- and *cis*-1-propenylbenzene with INCO according to published procedures[7] afforded **8a** and **8b**, respectively. The commercially available *threo*- and *erythro*-2-amino-1-phenyl-1-propanols were cyclized with $COCl_2$[3] to the corresponding **8c** and **8d**. Similarly, **8e** and **8f** were prepared from the amino alcohols obtained by ring opening of the appropriate aziridines which are easily accessible through *trans*-stilbene.[9] Treatment of the epoxide of allylbenzene with KOCN afforded **8g**.[10] Finally, 2-amino-1,1-diphenyl-1-propanol was prepared from propiophenone oxime and phenyl Grignard[11] and cyclized with $COCl_2$ to **10a**. N-Nitrosation of the stereochemically pure oxazolidones led to **9a-g** and **10b**, containing the characteristic 1800 cm^{-1} absorption.



8a, trans, R_1 = Ph; R_2 = Me
b, cis, R_1 = Ph; R_2 = Me
c, trans, R_1 = Me; R_2 = Ph
d, cis, R_1 = Me; R_2 = Ph
e, trans, R_1 = R_2 = Ph
f, cis, R_1 = R_2 = Ph
g, R_1 = H; R_2 = CH_2Ph



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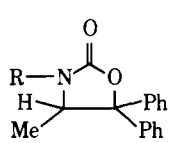


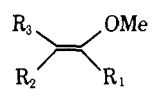
10a, R = H
b, R = NO

Exposure of 3-nitroso-*trans*-(4-phenyl-5-methyl)-2-oxazolidone (**9a**) to 1 equiv of NaOMe in methanol at 25° led to immediate evolution of N_2. Reaction was complete within 5 min and led to a variety of products. As indicated in Table I the desired vinyl ethers **11a** and **11b** were formed only in traces while carbonate or carbonate derived products (**12a,b**; **14a,b**; **15a,b**) were found in major amounts.

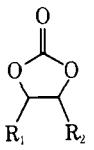
Table I
Products from Methoxide (1 equiv) Decomposition of 3-Nitroso-*trans*-(4-phenyl-5-methyl)-2-oxazolidone (9a) in Methanol

Product	Yield,[a] %	Derived from Scheme[b]
8a	9	V
11a + b	Trace	I
12a + b	23	IV
13	Trace	IV
14a	18	IV
14b	12	IV
15a + b	3	IV
16a	7	II
17a	15	II
17b	Trace	IV
Total	87	

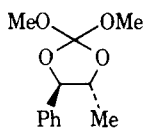
[a] See ref 12. [b] The products are assumed to be derived from **9** *via* Schemes I–V.



11a, R_1 = Ph; R_2 = Me; R_3 = H
b, R_1 = Ph; R_2 = H; R_3 = Me
c, R_1 = Me; R_2 = Ph; R_3 = H
d, R_1 = Me; R_2 = H; R_3 = Ph



12a, trans, R_1 = Ph; R_2 = Me
b, cis, R_1 = Ph; R_2 = Me
c, trans, R_1 = R_2 = Ph



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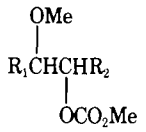
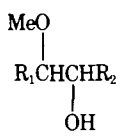
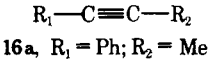


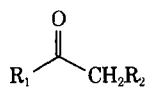
14a, erythro, R_1 = Ph; R_2 = Me
b, threo, R_1 = Ph; R_2 = Me
c, R_1 = Me; R_2 = Ph
d, erythro, R_1 = R_2 = Ph
e, threo, R_1 = R_2 = Ph
f, R_1 = H; R_2 = CH_2Ph



15a, erythro, R_1 = Ph; R_2 = Me
b, threo, R_1 = Ph; R_2 = Me
c, R_1 = Me; R_2 = Ph
d, erythro, R_1 = R_2 = Ph
e, threo, R_1 = R_2 = Ph
f, R_1 = H; R_2 = CH_2Ph



16a, R_1 = Ph; R_2 = Me
b, R_1 = R_2 = Ph
c, R_1 = H; R_2 = CH_2Ph



17a, R_1 = Ph; R_2 = Me
b, R_1 = CH_2Ph; R_2 = H
c, R_1 = R_2 = Ph

The quantitative estimation of the reaction products was carried out by gc on a 30% SE-30 column.[12]

All the products **11–16** were identified by either nmr comparison with authentic materials or a combination of nmr, ir, and mass spectra and elemental analysis. Some of the stereoisomers were isolated and analyzed only as a cis-trans or threo-erythro mixture (*e.g.*, **12, 15**).

Table II
Products from Methoxide Decomposition of 3-Nitroso-*trans*-(4-phenyl-5-methyl)-2-oxazolidone (9a) in Methanol as a Function of Methoxide Concentration

[OMe], equiv	8a	11a + b	12a + b	13	14a	14b	15a + b	16a	17a	17b	Total[a]	Ratio[b]	8a,[c] %
0.1	7	2	15	8	24	16		4	7		83	4.8	8
0.5	6	1	20	1	19	15	4	1	6	1	74	7.5	8
1.0	9		23		18	12	3	7	15		87	2.5	10
2.0	14		7	6	5	3	21		2		58	21	24

[a] See ref 12. [b] Ratio of products from Scheme IV to those from Schemes I and II; see Discussion. [c] Per cent **8a** in recovered product.

Table III
Products from Methoxide Decomposition of 3-Nitroso-*cis*-(4-phenyl-5-methyl)-2-oxazolidone (9b) in Methanol as a Function of Methoxide Concentration

[OMe], equiv	8b	11a + b	12a + b	13	14a	14b	15a + b	16a	17a	17b	Total[a]	Ratio[b]	8b,[c] %
0.1	8	2	20		17	12		4	15		78	2.3	10
0.5	10	6	17	1	19	12	4		2	2	73	6.9	14
1.0	13	1	3	9	8	7	8	7	10	3	69	2.1	19
2.0	14	2	3	9	5	3	6	5	7	4	68	2.9	21

[a] See ref 12. [b] Ratio of products from Scheme IV to those from Schemes I and II; see Discussion. [c] Per cent **8b** in recovered product.

Table IV
Products from Methoxide Decomposition (1 equiv) as a Function of Solvent for 3-Nitroso-*trans*-(4-phenyl-5-methyl)-2-oxazolidone (9a)

Solvent	8a	11a + b	12a + b	13	14a	14b	15a + b	16a	17a	17b	Total[a]	Ratio[b]	8a,[c] %
DMF	71		16		2						89		80
DMF–10% MeOH	12		46		10	3					71		17
Et_2O	50		24		1			1	7	2	85	3.5	59
Et_2O–10% MeOH	7		22	8	24	13	2	10	5	4	95	4.9	7
C_6H_6	52	4	26					3	5	1	91	2.2	57
C_6H_6–0.5% MeOH	44	2	29		2	1	1	5	4	2	90	3.2	49

[a] See ref 12. [b] Ratio of products from Scheme IV to those from Schemes I and II; see Discussion. [c] Per cent **8a** in recovered product.

Table V
Products from Methoxide Decomposition (1 equiv) as a Function of Solvent for 3-Nitroso-*cis*-(4-phenyl-5-methyl)-2-oxazolidone (9b)

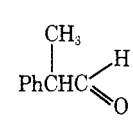
Solvent	8b	11a + b	12a + b	14a	14b	15a + b	16a	17a	17b	Total[a]	Ratio[b]	8b,[c] %
DMF	9	2	11					3	23	48	6.8	19
DMF–3% MeOH	9	1	11				8	8	21	58	1.9	16
Et_2O	33	1	23				3	3	8	71	4.4	46
Et_2O–0.5% MeOH	34	2	23	1	1	1	5	4	7	77	2.9	44

[a] See ref 12. [b] Ratio of products from Scheme IV to those from Schemes I and II; see Discussion. [c] Per cent **8b** in recovered product.

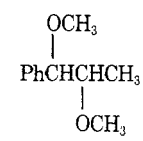
The decomposition of **9a** or **9b** required only catalytic amounts of methoxide ion. Although the composition of these product mixtures varied with changing NaOMe concentration (0.1–2 equiv) as shown in Tables II and III, the larger proportion of the mixture still consisted of carbonate derived products **12a,b**, **13**, **14a,b**, and **15a,b**. A mixture of stereoisomers, *e.g.*, **14a** and **14b**, was formed from stereochemically pure *N*-nitrosooxazolidone **9a** or **9b** regardless of methoxide ion concentration.

The effect of solvent on the decomposition of **9a** and **9b** with 1 equiv of NaOMe is shown in Tables IV and V. The most striking effect is an increasing amount of denitrosation of **9** to the parent oxazolidinone **8** on changing from methanol to aprotic solvents of varying polarity (ether, benzene, dimethylformamide). As expected, the yield of methoxy carbonate **14** was reduced. However, addition of increasing amounts of methanol to these aprotic solvents afforded increased yields of **14**.

The results observed on treatment of 3-nitroso-*trans*-(4 methyl-5-phenyl)-2-oxazolidone **9c** and its cis isomer **9d** with $NaOCH_3$ (1 equiv) in methanol (Tables VI and VII) were similar to those found for **9a** and **9b** except that 1-phenylpropyne (**16a**) was a major product and aldehyde **18** as well as diether **19** were now generated.



18



19

Methoxide-catalyzed decomposition of **9d** in methanol in the presence of a large excess of LiN_3 led to significant changes in the ratio of products although the relative amount of 1-phenylpropyne (**16a**) and phenylacetone (**17b**) was constant. A small amount (*ca.* 10%) of unidentified alkyl azide was obtained. Treatment of **9d** with an excess of sodium thiophenoxide in methanol produced carbonate **14c** as well as oxazolidone **8d** as the major products while no vinyl ether **11c** or **11d** was detected by gc.

Table VI
Products from Methoxide (1 equiv) Decomposition of 3-Nitroso-*trans*-(4-methyl-5-phenyl)-2-oxazolidone (9c) in Methanol

Product	Yield, %	From Scheme[a]
14c	11	IV
15c	7	IV
16a	32	II
17a	3	IV
17b	2	II
18	18	IV
19	15	III
Total	88	
Ratio of Scheme IV/ Schemes II and III		0.8/1

[a] See discussion.

Table VII
Products from Methoxide (1 equiv) Decomposition of 3-Nitroso-*cis*-(4-methyl-5-phenyl)-2-oxazolidone (9d) in Methanol

Product	Yield, %	From Scheme[a]
14c	16	IV
15c	5	IV
16a	30	II
17a	11	IV
17b	7	II
18	15	IV
19	9	III
Total	93	
Ratio of Schemes IV/ Schemes II and III		1/1

[a] See Discussion.

Table VIII
Products from Methoxide (1 equiv) Decomposition of 3-Nitroso-*trans*-(4,5-diphenyl)-2-oxazolidone (9e) in Methanol

Product	Yield, %	From Scheme[a]
12c	19	IV
14d + e	6	IV
15d + e	44	IV
16c	15	II
17c	13	II, IV
Total	97	
Ratio of Scheme IV/ Scheme II		5.5/1 to 2.8/1[b]

[a] See Discussion. [b] Range is due to the uncertainty of the origin of **17c**.

Table IX
Products from Methoxide (1 equiv) Decomposition of 3-Nitroso-*cis*-(4,5-diphenyl)-2-oxazolidone (9f) in Methanol

Product	Yield, %	From Scheme[a]
12c	1	IV
14d + e	18	IV
15d + e	28	IV
16c	32	II
17c	10	II, IV
Total	89	
Ratio of Scheme IV/ Scheme II		1.8/1 to 1.1/1[b]

[a] See Discussion. [b] Range is due to uncertainty of origin of **17c**.

Tables VIII and IX present data on the reaction of *trans*- and *cis*-3-nitroso-4,5-diphenyl-2-oxazolidones **9e** and **9f** with 1 equiv of sodium methoxide in methanol. Although diphenylacetylene (**16b**) was formed in large amounts, carbonates **12c**, **14d**, and **14e** and methoxy alcohols **15d** and **15e** were significant components of the product mixture.

Table X
Products from Methoxide (1 equiv) Decomposition of 3-Nitroso-5-benzyl-2-oxazolidone (9g) in Methanol

Product	Yield, %	From Scheme[a]
14f	4	IV
15f	11	IV
16c	25	II
17b	12	IV
20	41	III
Total	93	
Ratio of Scheme IV/ Schemes II and III		0.4/1

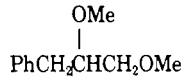
[a] See Discussion.

Table XI
Products from Methoxide (1 equiv) Decomposition of 3-Nitroso-4-methyl-5,5-diphenyl-2-oxazolidone (10b)

Product	Yield, %	From Scheme[a]
21a	48	I
21b	12	I
22	20	II, IV
23	11	IV
Total	91	
Ratio of Scheme IV/ Schemes I and II		0.5/1 to 0.14/1[b]

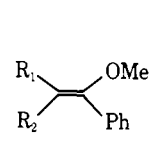
[a] See Discussion. [b] Range is due to uncertainty of origin of **22**.

Similar results were observed in the decomposition of **9g** (Table X), with 3-phenylpropyne (**16c**) and diether **20** being the major products.

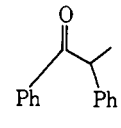


20

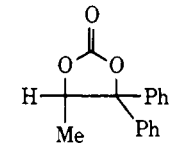
Vinyl ethers **21a** and **21b** were obtained as the major products from the reaction of 3 nitroso-2-oxazolidone **10b** with NaOMe (1 equiv) in methanol (Table XI). Only minor amounts of 2-phenylpropiophenone (**22**) and carbonate **23** were formed.



21a, R_1 = Me; R_2 = Ph
b, R_1 = Ph; R_2 = Me



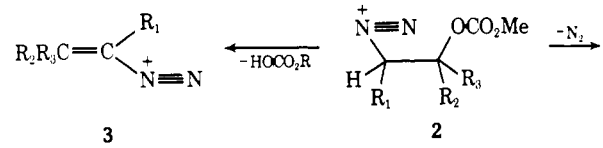
22



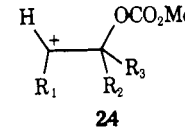
23

Discussion

Reaction Pathways. The products described above arise from two major pathways. Methoxide attacks **9** and **10b** at the carbonyl group to generate diazonium ion **2** which reacts further to afford **3** as shown in Scheme I or by loss of N_2 to yield **24**. While Newman[3,4] has shown that **3** (*via* cation **4**) reacts with alcohols to produce the



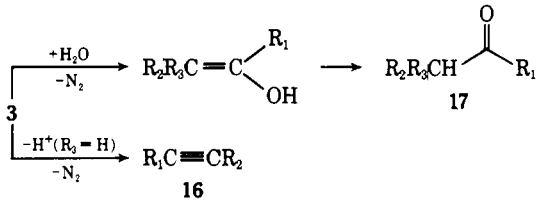
3 **2**



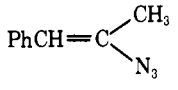
24

corresponding vinyl ethers (Scheme I), in the experiments described above only **10b** afforded products according to this pathway. The predominant reaction of **3** generated from **9a-g** was either loss of N_2 and H^+ (R_3 = H) to give an acetylene or loss of N_2 to generate a ketone *via* the enol (Scheme II).

Scheme II



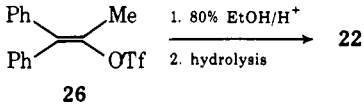
Although azide is a much better nucleophile than methoxide, and hydroxide, decomposition of **9d** in the presence of excess lithium azide failed to trap **3** as the desired vinyl azide **25**. The lack of solvent derived products **11** from **3** is



25

not totally surprising since Moss[13] has pointed out that unstable carbonium ions generated from diazotates rarely completely escape the solvent cage. Thus, **3** affords acetylenes **16** or ketones **17** before it can react with methanol to yield **5**.

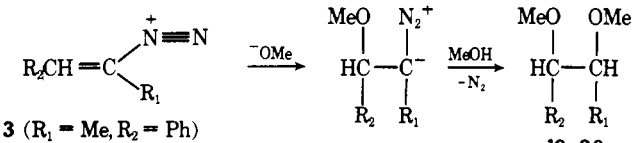
It is interesting to note in the one case where vinyl ethers were the major products (*i.e.*, **10b** → **21a** + **21b**) that rearrangement to the more stable vinyl cation was observed exclusively. Newman[4] has reported several examples of facile phenyl migrations in decompositions of **1**. More to the point is the observation by Schleyer[14] that triflate **26** on hydrolysis in 80% ethanol and acidic workup affords almost exclusively **22**.



26

When **3** was generated from **9c**, **9d**, and **9g**, a portion of the ion was attacked by methoxide at the carbon β to the diazonium function affording a diazo compound which reacted further with methanol to produce diethers **19** and **20** (Scheme III). Newman[4a] has suggested this pathway for the formation of a 1,2-diether from decomposition of **1** in methanol. A second possible pathway involving an SN1 or SN2 substitution of methoxide for carbonate (perhaps with methoxyl participation) on **14c** and **14f** is considered unlikely because similar compounds were not obtained from the other oxazolidones (**9**).

Scheme III

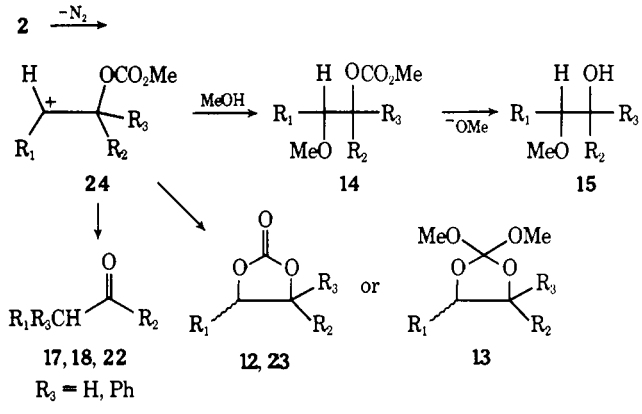


3 (R_1 = Me, R_2 = Ph)
(R_1 = H, R_2 = CH_2Ph)

19, 20

The second major pathway the reaction may take, if it does not proceed to **3** and its subsequent products, is to lose N_2 giving carbonium ion **24** which can yield a variety of products as shown in Scheme IV. Thus, attack by methanol produces methoxy carbonate **14**, which on further reaction with methoxide yields methoxy alcohol **15**. Intramolecular participation by carbonate generates compounds **12**, **13**, and **23**. Finally, migration of a hydrogen[15] or phenyl group leads to carbonyl compounds **17**, **18**, and **22**. Scheme IV is consistent with the results that Newman[16] has reported on the decomposition of 3-nitroso-4,4-disubstituted 2-oxazolidones with base and also with the studies of Moss[17] who has reported several thorough investigations of the chemistry of alkyl cations generated from alkyl diazotates related to **2**. In both cases the products were related to those described above.

Scheme IV



17, 18, 22
R_3 = H, Ph

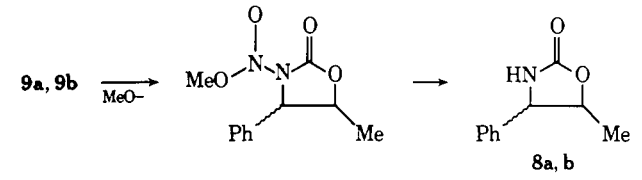
12, 23 **13**

That the formation of methoxy carbonates **14a**, **14b**, **14d**, and **14e** and of the derived methoxy alcohols **15a**, **15b**, **15d**, and **15e** is not due to an SN2 displacement on the N-bearing carbon of **2** but instead involves epimerizable species such as carbonium ion **24** is evident from the lack of stereospecificity in the transformations **9a** or **9b** → **14a** + **14b** and **9e** or **9f** → **14d** + **14e**. On the other hand, the conversion of the stereoisomeric **9c** and **9d** into the same products **14c** and **15c** suggests a solvent cage trapping of the carbonium ion **24** which is more reactive when R_1 is methyl rather than phenyl. This is also evident by the intramolecular carbonate participation in **24** to produce **12** and **13** when R_1 = Ph but not when R_1 = Me or H.

Recent work has suggested that thiophenoxide in methanol is quite effective in E2 eliminations.[18] Since the generation of **3** from **2** might be viewed as an E2 elimination (or E1cb), the decomposition of **9d** was carried out with 1 equiv of sodium thiophenoxide in methanol. However, no increase in products derived from **3** (*i.e.*, **11c**, **11d**, **16**, **17b**, or **18**) was detected, the major products being produced from **24**.

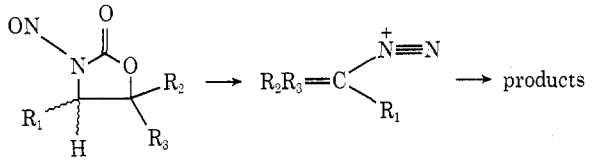
Occasionally, the reversible attack by methoxide at the N=O function competes successfully with attack at the carbonyl function and leads to denitrosation. Although it is not clear why only **9a** and **9b** were denitrosated (Scheme V) by methoxide, the reaction itself is not unusual. Jones and Muck[19] have reported that base attacks the nitroso group of *N*-nitroso-*N*-alkylurethane and -amides. The increase in denitrosated product in aprotic solvents as shown in Tables IV and V is consistent with observations made by Jones.[19] It is also interesting to note that, when **9d** was treated with azide and thiophenoxide,

Scheme V



8a, b

Table XII
Per Cent Yield of Vinyl Diazonium Ion Derived Products from Base Decomposition of 3-Nitroso-2-oxazolidones in Protic Solvents



1

Entry	R_1	R_2	R_3	Yield, %
1a[a-c]	H	Alkyl	Alkyl	70–85
1b[a,b]	H	H	Ph	65–90
1c[a]	H	Alkyl	Ph	90
1d[a]	H	Ph	Ph	100
1e[d]	Et	H	H	0
1f[d]	Ph	H	H	14
1g[a]	Ph	Ph	Ph	60
1h[b]	Me	9-Fluorenyl		85

[a] Reference 3. [b] Reference 4a. [c] Reference 4b. [d] Reference 16.

which are better nucleophiles than methoxide, denitrosation to **8d** occurred to a significant extent whereas this product was not observed with mathoxide alone.

Factors Which Determine Reaction Pathway. The predominant mode of reaction will be determined by the ease with which diazonium ion **2** loses alkyl carbonate to afford vinyldiazonium ion **3** relative to the ease with which it loses nitrogen to produce the saturated carbonium ion **24**. As would be expected, increasing substitution at C-4 of **1** would favor formation of **24** since it is well known that secondary diazotates lose N_2 much more readily than do primary diazotates.[20] The longer lifetime of a primary diazotate as obtained from **1** (R_1 = H) and the fact that such species are known to be in equilibrium with the corresponding diazo compound[20] increases the probability that **2** (R_1 = H) will produce the vinyl intermediate **3**.

The results described herein in conjunction with those of Newman (summarized in Table XII) indicate that the substitution pattern at C-4 of **1** is not the sole factor controlling the reaction. Thus, while 5,5-dialkyl systems afford products derived exclusively from **3** (**1a**, Table XII), only 70–75% of the products from the 5-monoalkyl **9g** were generated *via* **3**. Similarly, only a 12% yield of acetylene (*via* **3**) was obtained from the parent 3-nitrosooxazolidone.[3] That the substituents at C-5 influence the reaction can also be seen by comparing several of the results from Table XII with those from this study. Thus, in the cases of 4-monoalkyl substitution, 3-nitroso-4-ethyl-2-oxazolidone (**1e**, Table XII) afforded only carbonium ion (**24**) derived products, while decomposition of **9c** and **9d** (4-alkyl-5-phenyl substituted) resulted in about 50% of the products arising from **3**. In the presence of two aromatic substituents at C-5, **10b** afforded as much as 85% of the products *via* **3**,[21] and **1h** (Table XII) furnished products exclusively from this intermediate. Further examples can be drawn from the 4 phenyl substituted substrate from **1f** (Table XII) which generated only 15% of its products from **3**, while the products derived *via* **3** from **9a**, **9b**, **9e**, and **9f** (4-phenyl-5-alkyl or phenyl substituted) formed about 19, 29, 15–25, and 35–45% of the mixture, respectively. These results should be contrasted with the 4,5,5-triphenyl case **1g** (Table XII) which afforded products solely from **3**.

The above observations suggest two criteria in determining the partition of **2** between **3** and **24**.[22] If a stable carbonium ion cannot be formed by loss of N_2 from **2** and if the carbonate can act as a good leaving group, then **2** will yield predominantly **3**. However, if a relatively stable carbonium ion (**24**) can be generated by loss of N_2 or if the carbonate function is not readily lost, formation of **24** becomes competitive and may become exclusive. In summary, *if in 3-nitroso-2-oxazolidones* **1** *C-4 is primary, C-5 must be tertiary or benzylic in order to furnish a good yield of product derived from vinyl diazonium ion* **3**. *If C-4 is secondary or benzylic, then C-5 must be benzyhydrylic in order for decomposition through* **3** *to be the predominant path.*

In such cases (see Tables XI and XII) the ratio of products derived from Scheme IV (*via* carbonium ion **24**) *vs.* those derived from Schemes I, II, and III (*via* vinyl diazonium ion **3**) is at least less than 0.33. In the other cases (see Tables I–X) this ratio is usually larger than 1.

Experimental Section[23]

2-Oxazolidones. ***trans*-(4-Phenyl-5-methyl)-2-oxazolidone (8a)** was prepared from iodine isocyanate and *trans*-propenylbenzene according to published procedures.[7]

***cis*-(4-Phenyl-5-methyl)-2-oxazolidone (8b)** was prepared as above from *cis*-propenylbenzene.[7]

***trans*-(4-Methyl-5-phenyl)-2-oxazolidone (8c)** was prepared from *threo*-1-phenyl-1-amino-2-propanol (K & K Labs) and phosgene according to the method of Newman.[3]

***cis*-(4-Methyl-5-phenyl)-2-oxazolidone (8d)** was prepared as above[3] from *erythro*-1-phenyl-1-amino-2-propanol (Aldrich) and phosgene.

***trans*-(4,5-Diphenyl)-2-oxazolidone (8e).** *cis*-2,3-Diphenylaziridine was prepared from *trans*-stilbene according to published procedures.[9a,c] Treatment with aqueous sulfuric acid afforded *threo*-1,2-diphenyl-2-aminoethanol.[24] **8e** was obtained by cyclization with phosgene as above.[3]

***cis*-(4,5-Diphenyl)-2-oxazolidone (8f).** *trans*-Stilbene and iodine azide were combined to afford the corresponding iodo azide[9a] which was converted into *trans*-2,3-diphenylaziridine by reaction with trimethyl phosphite and reduction with lithium aluminum hydride.[9b] Treatment of the aziridine with aqueous sulfuric acid afforded *erythro*-1,2-diphenyl-2-aminoethanol.[24] Cyclization with phosgene as above[3] afforded **8f**

5-Benzyl-2-oxazolidone (8g) was prepared from 2,3-epoxy-1-phenylpropane (from allylbenzene and *m*-chloroperbenzoic acid) and potassium cyanate in dimethylformamide according to the procedure of Swern.[10]

4-Methyl-5,5-diphenyl-2-oxazolidone (10a). From propiophenone oxime and phenylmagnesium bromide was obtained 2-amino-1,1-diphenyl-1-propanol according to the method of Campbell.[11] Reaction with phosgene as above[3] afforded **10a**.

3-Nitroso-2-oxazolidones (9, 10b). General Procedure. The oxazolidone (1 equiv) dissolved in methylene chloride was added dropwise to a stirred mixture of solid sodium acetate (4 equiv) and nitrogen dioxide (3 equiv) in methylene chloride maintained in a Dry Ice bath. When addition was complete, the solution was warmed to 0°. After about 2 hr the solution was diluted with water and the layers were separated. The methylene chloride was washed with 5% $NaHCO_3$, aqueous ammonium chloride, and water and dried over $MgSO_4$. Evaporation of the solvent (no heat) afforded the product in 80–90% yield as a yellow solid or viscous oil.

Decomposition of 3-Nitroso-2-oxazolidones (9, 10b) in Methanol and Isolation of Products. To a methanolic (25–100 ml) solution of **9** or **10b** (0.5–3.5 g) was added dropwise with stirring over several minutes a solution of sodium methoxide (0.1–2.0 equiv) in methanol (10–50 ml). Evolution of nitrogen was spontaneous. The solution turned from yellow to orange. When the evolution of gas had stopped (<5 min), the solution was poured into several hundred milliliters of water and extracted with chloroform or ether. The extract was dried over $MgSO_4$ and concentrated to afford a crude product which was separated and analyzed by gas chromatography as described below.

Decomposition of 3-Nitroso-2-oxazolidones (9a,b) in Aprotic Media and Isolation of Products. Solid sodium methoxide was added all at once to a solution of **9a** or **9b** in the desired solvent. The mixture was stirred overnight and worked up as above. When DMF was the solvent, it was removed from the crude product by either repeated washings with water or high vacuum evaporation both of which resulted in loss of product.

Analysis of Products from 3-Nitroso-4-phenyl-5-methyl-2-

oxazolidones (9a,b). Products were isolated by preparative gc techniques and identified by comparison with authentic samples or by spectral data. Quantitative analyses of the mixtures were made by integration of the peak areas with no attempt to determine response factors. The optimum conditions were found to be a 20% SE-30 column on 60/80 Chromosorb W (6 ft × ¼ in.) operated at 160° for 5 min, 185° for 6 min, and 220° for 5 min with a flow rate of 60 ml of He/min and an injector temperature of 340°. The following products were obtained in order of increasing retention time as indicated.

1. (*E*)- and (*Z*)-1-methoxy-1-phenyl-1-propene (**11a,b**): identified by nmr;[25] 2.5 min.

2. 1-Phenylpropyne (**16a**): identified by comparison with authentic specimen; 3.3 min.

3. 1-Phenyl-2-propanone (**17b**): identified as above; 4.0 min.

4. 1-Phenyl-1-propanone (**17a**): identified as above; 4.6 min.

5. *erythro*- and *threo*-1-methoxy-1-phenyl-2-propanol (**15a,b**): nmr ($CDCl_3$) τ 2.65 (s, 5, Ph), 6.00 (m, 2, -CH), 6.75 (s, 3, OMe), 8.9 (d, 3, Me erythro isomer), 9.1 (d, 3, Me threo isomer); 6.4 min. *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.49; H, 8.36.

6. *erythro*-Methyl 2-(1-methoxy-1-phenyl)propyl carbonate (**14a**): ir ($CHCl_3$) 1750 cm^{-1} [ROCOOR]; nmr ($CDCl_3$) τ 2.6 (s, 5, Ph), 5.1 (m, 1, HCMe), 5.7 (d, 1, HCPh), 6.3 (s, 3, OMe), 6.7 (s, 3, OMe), 8.7 (d, 3, Me); 11.7 min. *Anal.* Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.07; H, 7.24.

7. *threo*-Methyl 2-(1-methoxy-1-phenyl)propyl carbonate (**14b**): nmr ($CDCl_3$) τ 2.6 (s, 5, Ph), 4.9 (m, 1, HCMe), 5.8 (d, 1, HCPh), 6.2 (s, 3, OMe), 6.8 (s, 3, OMe), 8.9 (d, 3, Me); 12.4 min.

8. 2,2-Dimethoxy-*trans*-(5-methyl-4-phenyl)-1,3-dioxolane (**13**): nmr ($CDCl_3$) τ 2.6 (m, 5, Ph), 5.2 (d, 1, HCPh), 5.9 (m, 1, HCMe), 6.5 (s, 3, OMe), 6.6 (s, 3, OMe), 8.7 (d, 3, Me); 12.8 min. *Anal.* Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.20; H, 6.96.

9. *cis*- and *trans*-(5-methyl-4-phenyl)-2-dioxolone (**12a,b**): ir (neat) 1800 cm^{-1} (dioxolone ring); nmr ($CDCl_3$) τ 2.6 (s, 5, Ph), 4.2 (d, 1, HCPh, trans isomer), 4.8 (d, 1, HCPh, cis isomer), 4.8 (m, 1, HCMe, cis isomer), 5.3 (m, 1, HCMe, trans isomer), 8.4 (d, 3, Me, trans isomer), 9.0 (d, 3, Me, cis isomer); 14.0 min. *Anal.* Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.54; H, 5.73.

10. 4-Phenyl-5-methyl-2-oxazolidone (**8a,b**): identified by comparison with authentic specimen; 16 min. **8a** was obtained from **9a** and **8b** from **9b**.

Analysis of Products from 3-Nitroso-4-methyl-5-phenyl-2-oxazolidones (9c,d). The products were separated and analyzed as above. A 30% SE-30 on Chromsorb W column (⅜ in. × 30 ft) was employed with a flow rate of 200 ml of He/min and an injector temperature of 350°. The column temperature was raised from an initial temperature of 190 to 290° at 10°/min. The following products were obtained in order of increasing retention time.

1. 1-Phenylpropyne (**16a**): identified by comparison with authentic specimen; 7 min.

2. 2-Phenylpropanal (**18**): identified as above; 7.6 min.

3. 1-Phenyl-2-propanone (**17b**): identified as above; 8.2 min.

4. 1-Phenyl-1-propanone (**17a**): identified as above; 8.6 min.

5. 1,2-Dimethoxy-1-phenylpropane (**19**): nmr ($CDCl_3$) τ 2.7 (s, 5, Ph), 5.6 (d, 1, HCPh), 6.65 (s, 3, OMe), 6.75 (s, 3, OMe), 7.0 (m, 1, HCMe), 8.7 (d, 3, Me); 9.8 min. *Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.37; H, 8.95.

6. 1-Phenyl-2-methoxy-1-propanol (**15c**): nmr ($CDCl_3$) τ 2.65 (s, 5, Ph), 5.1 (d, 1, HCPh), 6.6 (s, 3, OMe), 7.2 (m, 1, HCMe), 9.0 (d, 3, Me); mass spectrum (70 eV) *m/e* 166 (M^+), 107 [PhC(OH)H], 59 [$CH_3C(OMe)H$]; 10.5 min.

7. Methyl 1-(1-phenyl-2-methoxy)propyl carbonate (**14c**): ir ($CHCl_3$) 1750 cm^{-1} (ROCOOR), nmr ($CDCl_3$) τ 2.6 (s, 5, Ph), 4.4 (d, 1, HCPh), 6.2 (s, 3, OMe), 6.6 (s, 3, OMe), 6.3 (m, 1, HCMe), 9.0 (d, 3, Me); mass spectrum (70 eV) *m/e* 224 (M^+), 149 [$CH(Ph)CH(OMe)CH_3^+$], 75 ($MeOCO_2^+$), 59 [$CH_3C(OMe)H$]; 13.0 min.

Decomposition of 9d in Excess Lithium Azide. To a solution of 13.4 g (274 mmol) of lithium azide in 75 ml of methanol was added 1.6 g (7.7 mmol) of **9d**. To the stirred solution was added dropwise 10 ml of methanol which had been treated with 0.2 g (8.7 mmol) of sodium. Work-up as above afforded 1.0 g of yellow amorphous solid. The infrared spectrum contained a strong azide band at 2100 cm^{-1}. However, column chromatography with Skellysolve B as eluent afforded only 1-phenylpropyne (**16a**).[26] The following products were observed upon gas chromatography using the above conditions: 19% 1-phenylpropyne (**16a**), 14% 1-phenyl-2-propanone (**17b**), 11% 1-phenyl-1-propanone (**17a**), 7% 1-phenyl-2-methoxy-1-propanol (**15c**), and 14% **8d** all identified by comparison with authentic samples. Two smaller peaks were noted, one of which was an alkyl azide (about 10%) and the second possibly a vinyl ether (**11c** or **11d**) in about 5% yield. However, no evidence for 1-phenyl-2-azido-1-propene (**25**) was noted.

Decomposition of 9d in Methanol with Excess Sodium Thiophenoxide. Thiophenol (2 g, 182 mmol) was added to 20 ml of methanol which had been treated with 0.43 g (187 mmol) of sodium. This solution was added dropwise to a stirred solution of 1.9 g (92 mmol) of **9d** in 75 ml of methanol. Work-up as above afforded a chloroform–ether extract which was washed with 5% KOH to remove excess thiophenol. After drying over magnesium sulfate and concentration *in vacuo*, 2.36 g of yellow viscous oil was obtained. The reaction mixture was analyzed by gc using the above conditions. The major products were carbonate **14c**, **8d**, and three large unidentified peaks with retention times longer than **8d**. No 1-phenyl-2-propanone (**17b**) was observed and only a trace of 1-phenylpropyne (**16a**) was noted.

Analysis of Products from 3-Nitroso-4,5-diphenyl-2-oxazolidones (9e,f). Experiment was carried out as above except that column temperature was maintained at 310°. The following products were obtained in order of increasing retention time.

1. 1,2-Diphenylacetylene (**16b**): identified by comparison with authentic specimen; 7.8 min.

2. 1,3-Diphenyl-2-propanone (**17c**): identified as above; 8.8 min.

3. 2-Methoxy-1,2-diphenylethanol (**15d,e**): nmr ($CDCl_3$) τ 2.7 (m, 10, Ph), 5.0 (d, 1, CH, threo), 5.3 (d, 1, CH, erythro), 5.6 (d, 1, CH, threo), 5.9 (d, 1, CH, erythro), 6.6 (s, 3, OMe, erythro), 6.7 (s, 3, OMe, threo); mass spectrum (70 eV) *m/e* 210 ($M^+ - H_2O$), 178 (PhC≡CPh), 121 [PhC(OMe)H], 107 [PhC(OH)H]; 9.3 min.

4. Methyl 1-(2-methoxy-1,2-diphenyl) ethyl carbonate (**14d,e**): ir ($CHCl_3$) 1750 cm^{-1} (ROCOOR); nmr ($CDCl_3$) τ 2.7 (m, 10, Ph), 4.2 (d, 1, $HCOCO_2Me$), 5.4 (d, 1, HCOMe), 6.2 (s, 3, OMe, erythro), 6.3 (s, 3, OMe, threo), 6.7 (s, 3, OMe, erythro), 6.8 (s, 3, OMe, threo); 11.3 min. *Anal.* Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.59; H, 6.44.

5. *trans*-(4,5-Diphenyl)-2-dioxolone (**12c**): ir ($CHCl_3$) 1800 cm^{-1} (dioxolone ring); nmr ($CDCl_3$) τ 2.5 (s, 10, Ph), 4.5 (s, 2, CH); 17.8 min. *Anal.* Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.85; H, 5.13.

Analysis of Products from 3-Nitroso-5-benzyl-2-oxazolidone (8g). Experimental details are identical with those used for **9c,d** above. The following products were obtained in order of increasing retention times.

1. 3-Phenyl-1-propyne (**16c**): identified by nmr;[27] 6.1 min.

2. 1-Phenyl-2-propanone (**17b**): identified by comparison with authentic specimen; 8.2 min.

3. 1,2-Dimethoxy-3-phenylpropane (**20**): nmr ($CDCl_3$) τ 2.7 (s, 5, Ph), 6.5 (m, 3, CH, CH_2), 6.6 (s, 3, OMe), 6.65 (s, 3, OMe), 7.15 (d, 2, CH_2Ph); mass spectrum (70 eV) *m/e* 180 (M^+), 148 ($M^+ - MeOH$), 135 [$-CH(OMe)CH_2Ph$], 89 [$-CH(OMe)-CH_2(OMe)$]; 10.9 min.

4. 1-Methoxy-3-phenyl-2-propanol (**15f**): nmr ($CDCl_3$) τ 2.7 (s, 5, Ph), 6.4 (m, 3, CH, CH_2), 6.6 (s, 3, OMe), 7.15 (d, 2, CH_2Ph); 11.4 min. *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.34; H, 8.61.

5. Methyl 2-(1-methoxy-3-phenyl)propyl carbonate (**14f**): ir ($CHCl_3$) 1750 cm^{-1} (ROCOOR); nmr ($CDCl_3$) τ 2.7 (s, 5, Ph), 5.0 (m, 1, CH), 6.25 (s, 3, OMe), 6.55 (d, 2, CH_2OMe), 6.6 (s, 3, OMe), 7.0 (d, 2, CH_2Ph); mass spectrum (70 eV) *m/e* 192 ($M^+ - MeOH$), 149 [$PhCH_2CH(OMe)CH_2^-$], 133 [$-CH(OCO_2Me)-CH_2(OMe)$], 45 (CH_2O^+Me); 14.4 min.

Analysis of Products from 3-Nitroso-4-methyl-5,5-diphenyl-2-oxazolidone (10b). Experiment was performed as above with column temperature raised from 300 to 325° at 1°/min. The following products were obtained in order of increasing retention time.

1. (*E*)-1-Methoxy-1,2-diphenyl-1-propene (**21a**): nmr ($CDCl_3$) τ 2.85, 2.90 (2 s, 10, Ph), 6.55 (s, 3, OMe), 7.8 (s, 3, Me); 9.6 min. *Anal.* Calcd for $C_{16}H_{16}O$: C, 85.65; H, 7.20; O, 7.15. Found: C, 85.47; H, 7.24.

2. (*Z*)-1-Methoxy-1,2-diphenyl-1-propene (**21b**): nmr ($CDCl_3$) τ 2.60 (m, 10, Ph), 6.75 (s, 3, OMe), 8.05 (s, 3, Me); mass spectrum (70 eV) *m/e* 224 (M^+); 11.0 min.

3. 2-Phenylpropiophenone (**22**): ir ($CHCl_3$) 1680 cm^{-1} [PhC(=O)-]; nmr ($CDCl_3$) τ 2.0 (m, 2, ortho H's of PhCO), 2.75 (m, 8, Ph), 5.30 (q, 1, CH, J = 7.0 Hz), 8.5 (d, 3, CH_3, J = 7.0 Hz); mass spectrum (70 eV) *m/e* 209 ($M^+ - 1$), 105 ($PhCO^+$); 11.3 min.

4. 4-Methyl-5,5-diphenyl-2-dioxolone (**23**): ir ($CHCl_3$) 1800 cm^{-1} (dioxolone ring); nmr ($CDCl_3$) τ 2.50 (s, 5, Ph), 2.70 (m, 5, Ph), 4.5 (q, 1, CH, J = 6.7 Hz), 8.80 (d, 3, CH_3, J = 6.7 Hz); mass spectrum (70 eV) *m/e* 254 (M^+), 253 ($M^+ - 1$), 167, 166, 165, 105, 77; 21.8 min.

Acknowledgment. Support of this research by Grant GP-36271X from the National Science Foundation is gratefully acknowledged.

Registry No. 8a, 19901-85-0; **8b,** 19901-86-1; **8c,** 28044-23-7; **8d,** 28044-22-6; **8e,** 19190-95-5; **8f,** 19202-66-5; **8g,** 42746-49-6; **9a,** 42746-62-3; **9b,** 42746-63-4; **9c,** 42746-64-5; **9d,** 42746-65-6; **9e,** 42746-66-7; **9f,** 42746-67-8; **9g,** 42746-50-9; **10a,** 42746-51-0; **10b,** 42746-52-1; **12a,** 42746-68-9; **12b,** 42746-69-0; **12c,** 28521-60-0; **13,** 42746-71-4; **14a,** 42746-72-5; **14b,** 42746-73-6; **14c,** 42746-53-2; **14d,** 42746-74-7; **14e,** 42746-75-8; **14f,** 42746-54-3; **15a,** 42746-76-9; **15b,** 42746-77-0; **15c,** 42746-55-4; **15d,** 6941-71-5; **15e,** 42746-79-2; **15f,** 32017-83-7; **19,** 42746-57-6; **20,** 42746-58-7; **21a,** 42746-80-5; **21b,** 42746-81-6; **22,** 2042-85-5; **23,** 42746-60-1.

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(21) While there is no proof available, it is felt that the majority of **22** is generated from **3** *via Scheme II. In the reactions of* **9a–d** and **9g** where significant amounts of carbonyl products were obtained from rearrangement of **24** (Scheme IV), equivalent amounts of methoxy carbonates **14** or methoxy alcohols **15** were observed. This was not the case with **10b**; thus it seems likely that **10b** produced only a small amount (15%) of **24** which afforded almost exclusively **23** and not **22**. In any case, at least 66% of the products were derived from **3**.
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Notes

Photoelectron Spectra of 1,4-Dihydropyridine and *N*-Methyl-1,4-dihydropyridine

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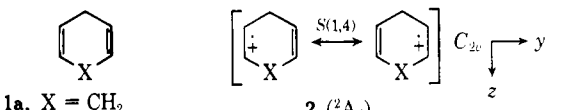
Received October 10, 1973

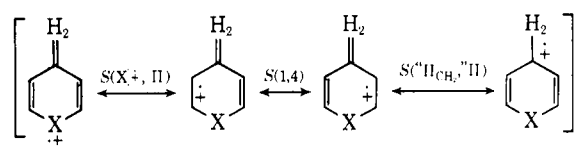
We wish to report the results of our investigation of the photoelectron spectra of 1,4-dihydropyridine (**1c**) and its *N*-methyl derivative (**1d**). Good synthetic methods for the preparation of these compounds were recently made available through the work of Fowler.[1] *N*-Carbomethoxy-1,4-dihydropyridine (**1b**) was obtained[1] by sodium borohydride reduction of *N*-carbomethoxypyridinium chloride and was easily purified by vacuum distillation. Pure samples of the N-H (**1c**) and N-CH_3 (**1d**) compounds were obtained by treatment of **1b** with methyllithium or lithium aluminum hydride[1] followed by careful vacuum distillation through an ice-jacketed Vigreux column.



1a, X = CH_2
b, X = NCO_2CH_3
c, X = NH
d, X = NCH_3

2 ($^2A_2$)

$$\Psi(^2A_2) = (1/\sqrt{2})[\Psi(ene_1) - \Psi(ene_2)]$$



3 ($^2B_1$)

$$\Psi(^2B_1) = a[\Psi(ene_1) + \Psi(ene_2)] - b\Psi(CH_2) - c\Psi_x(X)$$

The photoelectron spectra [He(I)] are shown as Figure 1.[2] One of the most striking features of the three spectra is the nearly identical position of the second band (a vertical ionization potential of 9.77 ± 0.05 eV for **1a**, **1c**, and