Aliphatic Azoxy Compounds. VI. Photolytic Isomerization of Azoxyalkanes and the Thermal Ring Opening of 2-Cyclohexyl-3-methyloxadiaziridine[1]

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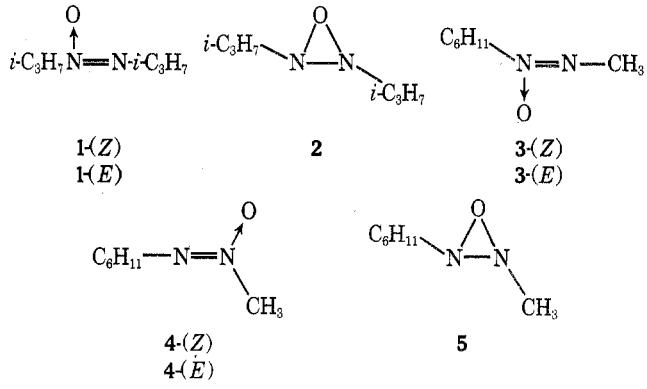
The photolysis of (*Z*)-bis(1-methylethyl)diazene *N*-oxide [1-(*Z*)] gave ring closure to oxadiaziridine **2** as the principal product accompanied by minor amounts of deoxygenation. Azoxyalkane 1-(*E*) was not obtained by direct photolysis of 1-(*Z*) owing to an unfavorable photoequilibrium strongly favoring 1-(*Z*); 1-(*E*) was obtained by thermolysis of **2** and, alternately, by peroxy acid oxidation of (*Z*)-azoisopropane. (*Z*)-Cyclohexylmethyldiazene 1-oxide [3-(*Z*)] and (*Z*)-methylcyclohexyldiazene 1-oxide [4-(*Z*)] gave both *Z* to *E* isomerization to their respective *E* isomers as well as ring closure to (*E*)-2-cyclohexyl-3-methyloxadiaziridine (**5**). The thermal ring opening of **5** was observed to give all four azoxyalkane isomers, 3-(*Z*) > 4-(*Z*) > 3-(*E*) > 4-(*E*), the ratios of which are determined principally by steric factors attending the ring opening. Acid catalysis of the ring opening of **5** (excess boron trifluoride etherate) enhances the yield of isomers **4**. Spectra and some properties of the *E* azoxyalkanes are discussed.

The photochemical reactions of the azoxy functional group have been studied in some detail[2] since Wacker's original observations in 1901[3] that 1,1′-azoxynaphthalene formed a red "oxy-azo" compound upon exposure to sunlight. Disregarding fragmentation[2] three types of reactions are found to occur: (1) deoxygenation to an azo compound via a triplet state;[4] (2) *Z*–*E* interconversion,[5] probably via a singlet state; (3) oxygen migration as manifested by (a) the formation of ortho (and para)[2,5c] hydroxyazoaryl compounds—the "photo-Wallach" rearrangement—and (b) oxadiaziridine formation[5d,6] or N to N′ oxygen migration[5e] which must proceed by way of the thermal ring opening of an oxadiaziridine intermediate. We have been interested in the oxadiaziridine-formation reaction for the purpose of preparing and firmly characterizing azoxyalkanes with *E* stereochemistry.[5e,f,7] In this paper we report on the photolytic isomerization of three azoxyalkanes, on some spectral aspects of three *E* azoxyalkanes, and on the thermal and acid-catalyzed ring openings of two oxadiaziridines.[10]

Photolyses. Small-scale test photolyses of azoxyalkane 1-(*Z*) indicated that irradiation at wavelengths above 300 nm (Pyrex low-wavelength cutoff) gave no reaction. In contrast, irradiation with a medium-pressure mercury lamp using a quartz reaction vessel resulted in the conversion of 1-(*Z*) to a new substance, with much shorter VPC retention time, which subsequently was shown to be oxadiaziridine **2**. In contrast with previous work with aryl–alkyl azoxy compounds,[5e] azoxyalkane 1-(*Z*) gave no 1-(*E*) upon irradiation. A preparative scale photolysis of 1-(*Z*) in pentane at ~10° for 17 h (with a Vycor filter to reduce decomposition, low-wavelength cutoff 210 nm) gave, by VPC analysis, 52% of **2**, 20% of recovered 1-(*Z*), and 28% of other compounds including (*Z*)- and (*E*)-azoisopropane, as well as some 1-(*E*) (produced by the ring opening of **2**). Oxadiaziridine **2** could be purified adequately by low-temperature distillation or column chromatography, but preparative VPC gave the purest samples.

The structure of **2** was indicated by the relatively high-field location of the α-CH NMR signal (entry 4, Table II) and by the thermal isomerization of **2** to 1-(*Z*) and 1-(*E*). Interestingly, the NMR signal of the β-methyl groups of **2**, which appeared as a sharp doublet in CCl_4, was split into a pair of doublets in the solvents acetone-d_6 and benzene (entries 5 and 6, Table II). 1,2-Diisopropyldiaziridine[11] also shows magnetically nonequivalent methyl groups, a fairly common observation for an isopropyl group bound to an asymmetric center,[12] but the solvent dependency of such nonequivalence was not observed for diaziridines.[11] The fact that **2** displays nonequivalent methyl groups means



that the isopropyl groups are bound to noninverting N atoms, a process which, in the cases of the companion *E* oxaziridine[13,14] and *E* diaziridine[14] ring systems, has an activation energy greater than 25 kcal mol^{-1}.

Azoxyalkane 1-(*E*) (with the isopropyl groups in a cis geometry) was initially prepared by peroxy acid oxidation of (*Z*)-azoisopropane. In contrast with 1-(*Z*), irradiation of 1-(*E*) at 350 nm did produce a reaction, namely conversion to 1-(*Z*). After 9 h a 1-(*Z*)/1-(*E*) ratio of 32 was obtained as determined by VPC analysis with no other products being observed. When an irradiation of 1-(*E*) in a quartz reaction vessel was monitored by VPC analysis, it was seen that *E* to *Z* conversion proceeded more rapidly than (and probably preceded) ring closure to **2**. VPC analysis of this reaction after 8 h showed ~2% of 1-(*E*), 82% of 1-(*Z*), and 16% of oxadiaziridine **2**. Thus, the high *Z*/*E* ratios observed in these photolyses of azoxyalkane 1-(*E*) indicate why no 1-(*E*) was observed in the photolyses of 1-(*Z*): the photoequilibrium concentration of 1-(*Z*) must be near 100%.

This high *Z*/*E* photoequilibrium ratio for azoxyalkanes **1** must reflect an unfavorable steric effect for formation of the *E* isomer of **1**, since direct *Z* to *E* conversion was effected by the photolyses of both 3-(*Z*) and 4-(*Z*). The photolyses of 3-(*Z*) and 4-(*Z*) were studied on both small and preparative scales using a medium-pressure Hg lamp and these latter results are summarized in Table I.[15] Thus, we see that isolable yields of 3-(*E*) and 4-(*E*) are produced from the corresponding *Z* isomers. To be sure, the relatively high yields are in part due to the low solubility of the *E* azoxyalkanes in alkane solvents, a factor which makes their preparation particularly convenient. However, when 3-(*Z*) was photolyzed in CD_3OD in which the *E* isomer is soluble, NMR analysis after 9.5 hr indicated that about 12% of 3-(*E*) was present, along with a low percentage of **5**.[16] This experiment also indicated that *Z*–*E* interconversion is fast-

Table I. Product Distribution after 2.5-h Photolysis of 3-(*Z*) and 4-(*Z*) in Pentane at −30°

Starting azoxyalkane	Products, % yield				
	3-(*Z*)	3-(*E*)	4-(*Z*)	4-(*E*)	5
3-(*Z*)	33[a]	28.5[b]	5	2.5	27[c]
4-(*Z*)	6	Trace	7[a]	19[b]	58[c]

[a] Isolated yield of recovered starting material accompanied by a lower percentage of the alternate *Z* isomer (as determined by NMR analysis). [b] Isolated by filtration of the reaction mixture and accompanied by a low percentage of the alternate *E* isomer (as determined by NMR analysis). [c] Isolated yield with purity >90%.

er than ring closure for compounds **3** in methanol, and the 12% yield is probably close to the *Z*–*E* photoequilibrium concentration of 3-(*E*). In comparison, the *Z*/*E* ratio at (or near) the rapidly established *Z*–*E* photoequilibrium for the phenyl counterpart of **3**, namely *N*-phenyl-*N'*-methyldiimide *N*-oxide, is 0.72.[5e] As the data of Table I indicates, azoxyalkane 4-(*Z*) was more readily converted to oxadiaziridine **5** than was 3-(*Z*). This photoreaction was most often used for preparations of **5**, which could be isolated by low-temperature chromatography or fractional distillation. The characterization of **5** rests on the relatively high field position of the prominent NMR signal of the *N*-methyl group, δ_{Me_4Si} ($CDCl_3$) 2.60 (singlet), and also on the thermal conversion of **5** to the four azoxyalkane isomers **3** and **4**.

We have formulated the oxadiaziridines **2** and **5** as *E* diastereomers. In this present work and in the work of Greene and Hecht[6] only a single oxadiaziridine was isolated from a given reaction. All known oxadiaziridines, including Greene's first[6a] di-*tert*-butyl example, have displayed approximately the same thermal stability toward ring opening. The only reasonable geometry for 2,3-di-*tert*-butyloxadiaziridine is *E*, and it is on the basis of this argument that we assign the *E* stereochemistry to **2** and **5**.

Structures and NMR Properties of *E* Azoxyalkanes. All three *E* azoxyalkanes, 1-(*E*), 3-(*E*), and 4-(*E*), had elemental analyses in agreement with the proposed structures, and all three were isomerized to the corresponding *Z* isomers. Thus, as mentioned above, photolysis of 1-(*E*) at 350 nm cleanly converted it to 1-(*Z*) which was identified by VPC analysis. Further, 4-(*E*) (mp 141°) was smoothly isomerized to 4-(*Z*) at 138° (refluxing *p*-xylene, $t_{1/2}$ ~50 min), and it was found that the isomerization of 3-(*E*) (mp 98°) was acid catalyzed, with 1 equiv of boron trifluoride etherate in benzene effecting the conversion to 3-(*Z*) at room temperature. Finally, the *E* geometry of 3-(*E*) and 4-(*E*) has been confirmed by single-crystal x-ray diffraction studies.[17]

Decoupling experiments on 1-(*E*) and 1-(*Z*) established that the lower field methine proton was coupled with the lower field methyl group doublet in each compound, a result which was duplicated with 1-(*E*) in the presence of $Eu(DPM)_3$. Further, the order of Lewis basicity toward $Eu(DPM)_3$ is 1-(*E*) > 1-(*Z*) ≫ **2** and, in fact, a threefold excess of 1-(*Z*) over 1-(*E*) was required before successful competition of the 1-(*Z*) isomer for a limited amount of $Eu(DPM)_3$ became evident. Also, since the proximal protons of **1** experienced the greater deshielding, the coordination site of $Eu(DPM)_3$ would appear to be the azoxy oxygen atom, rather than the distal N atom for this compound.

The chemical shifts of compounds **1**–**4** are recorded in Table II. A recent theoretical analysis[18] of azoxyalkane proton chemical shifts has for the first time allowed intelligent rationalization of the rather complex interplay of factors, including molecular conformation, which operate to determine the chemical shift of a given proton. At present,

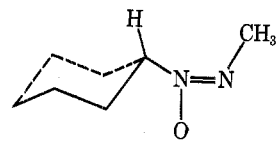
Table II. NMR Proton Chemical Shifts (δ) for Compounds 1–4

Entry	Compd	Solvent	Proximal[a] α	Proximal[a] β	Distal[a] α	Distal[a] β
1	1-(*Z*)	CCl_4	4.38[b]	1.42[b]	4.12	1.11
2	1-(*E*)	C_6H_6	4.33	1.22	4.29	1.18
3	1-(*E*)	CCl_4	4.96	1.41	4.10	1.25
4	2	CCl_4	2.15[c]	1.13[c]		
5	2	CD_3COCD_3	2.19	1.13 1.10[d]		
6	2	C_6H_6	2.25	1.15 0.98[d]		
7	3-(*Z*)	$CDCl_3$	4.14[e]		3.10[f]	
8	3-(*Z*)	C_6D_6	4.12		3.16	
9	3-(*E*)	$CDCl_3$	4.55		3.51	
10	3-(*E*)	C_6D_6	4.19		3.02	
11	4-(*Z*)	$CDCl_3$	4.02		3.98	
12	4-(*Z*)	C_6D_6	3.51		4.14	
13	4-(*E*)	$CDCl_3$	4.16		3.60	
14	4-(*E*)	C_6D_6	3.49		3.05	

[a] Defined as follows: proximal-HC_β—HC_α—N(O)=N—CH_α—CH_β. [b] H-α's of **1** were symmetrical septets, J = 6.5 Hz, and H-β's were doublets. J = 6.5 Hz. [c] Little or no effect was seen with 0.06 equiv of $Eu(DPM)_3$ added. [d] Two doublets were observed for the β-CH_3 groups (see text). [e] Signals for methine hydrogens of **3** and **4** were broad, unresolved multiplets. [f] Signals for methyl group hydrogens of **3** and **4** were singlets.

about all that can be reliably predicted, however, is that a given proton situated above the plane of an azoxy functional group will be shielded relative to that same proton in the plane of the azoxy group.[5e,19] Some unusual facets of azoxyalkane proton chemical shifts have already been noted.[20] Also puzzling is that, in $CDCl_3$, a substantial downfield shift is observed for all protons upon *Z* to *E* isomerization, *except* for the distal α-H of **4**, which is shifted upfield (compare entry 7 with 9, and entry 11 with 13, Table II).

If the solid state conformations **6** and **7**[17] are used as solution models for 3-(*E*) and 4-(*E*), respectively, then the



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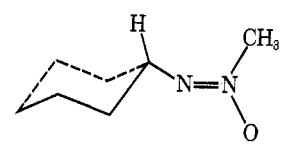

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benzene-induced shifts of the resonances of **3** and **4** are consistent with Williams' generalizations[21] about such phenomena. Thus, in the *Z* isomers the benzene solvent shifts the proximal H signals upfield while the distal H signals move downfield (compare entry 7 with 8 and entry 11 with 12, Table II). With the *E* isomers the signals for both proximal and distal protons are shifted upfield (compare entry 9 with 10 and entry 13 with 14, Table II). According to Williams, the benzene solvent molecule will probably be oriented in a nonplanar collision complex with the positive charge of a local dipole in such a fashion that the benzene ring lies away from the negative end of the dipole. With the aid of molecular models, Williams' generalizations are plausibly applied to the present cases. The steric bulk of the C_6H_{11} group of 3-(*Z*) produces a looser association with benzene than does the $CH_3N(O)$ grouping of 4-(*Z*). Hence, the solvent-induced shifts in 3-(*Z*) (in both directions) are of smaller magnitude. Also, models suggest that the distal protons of the *Z* isomers would, at a given moment, be located near the deshielding region of an associated benzene molecule. The *E* isomers, with their stronger dipole moment, form a stronger association complex with benzene. The geometry change apparently moves (and molecular

Table III. First-Order Rate Constants for the Thermal Rearrangement of Oxadiaziridine 5

Solvent	E_T[a]	ϵ[b]	Temp, °C	$k \times 10^{-4}$, sec^{-1}[c]	$t_{1/2}$, min
CD_3OD	55.5	32.6	40.5	6.71 ± 0.34[d]	18
			30.0	1.56 ± 0.14	75
			21.0	0.52 ± 0.11[d]	229
CD_3CN	46.0	36.2	40.5	6.10 ± 0.12	19
			21.0	0.68 ± 0.07[d]	173
C_6H_6	34.5	2.28	40.5	4.78 ± 0.19	24
CCl_4	32.5	2.23	40.5	3.03 ± 0.05	38
			21.0	0.26	446

[a] Reference 22. [b] Reference 23. [c] Average of two runs unless otherwise noted; uncertainties shown as standard errors, S_m. [d] Average of three runs.

models suggest this, also) the distal alkyl group to a position more directly above the benzene ring plane and into the shielding region of the benzene molecule in the complex. The steric effect of the $C_6H_{11}N(O)$ grouping is still evident, however, in that 3-(*E*) experiences smaller solvent shifts than does 4-(*E*).

Thermal Ring Opening of Oxadiaziridines. The thermal ring opening of oxadiaziridine **2** in several solvents has been reported by us previously.[5d] At that time it was noted that solvents of higher dielectric constant enhanced the yield of 1-(*E*), the more polar product, but with the best yield, the *E* isomer was still the minor product at 33%. Also, solvents of higher polarity caused a modest enhancement of the rate of ring opening.

With the unsymmetrically substituted oxadiaziridine **5** we have studied the kinetics of the ring-opening reaction in several solvents and have made an analysis of the products formed. It was our hope to be able to accurately monitor the rate of disappearance of the distinctive methyl NMR singlet of oxadiaziridine **5** and also accurately measure, by means of methyl singlet integration, the ratios of the product azoxyalkanes. However, as can be seen from Table II, there is overlapping of methine and methyl signals which complicated the analysis of product ratios [e.g., the proximal methine H of 3-(*Z*) and proximal CH_3 of 4-(*E*) have nearly the same chemical shift in $CDCl_3$ (entries 7 and 13, Table II)]. We took advantage of the substantial solvent-induced signal shifts observed for these compounds and arrived at an optimal method of employing a mixed solvent of benzene and the reaction solvent in a 3:1 by volume ratio for NMR analysis. However, even under these conditions, the broad absorption of the distal methine H of 4-(*E*) came underneath the CH_3 group absorptions of 3-(*Z*) and 3-(*E*). This necessitated the use of a correction factor, approximated by subtracting ⅓ of the integration value of the proximal methyl singlet of 4-(*E*) from the total integration of the 3-(*Z*) and 3-(*E*) methyl singlets. The ratio of 3/4 thus calculated tallied with that same ratio determined by VPC analysis under conditions which isomerized both *E* azoxyalkanes to their *Z* counterparts. However, we were not able to measure the product ratios as accurately as we desired, and accordingly have approached the interpretation of these results with some caution.

The rate constants determined in four solvents for the disappearance of **5** are collected in Table III. Qualitatively, the rate of ring opening is dependent upon the solvent parameter, E_T[22], not the dielectric constant of the solvent. The rate constants determined in CCl_4 at 21° showed an unexplained, systematic drift to lower value as the reaction progressed. The measurements made at the higher temperature were better behaved. The data collected at three temperatures in CD_3OD allowed the calculation of the activation parameters for the ring-opening reaction: E_a = 24.1 ± 0.3 kcal mol^{-1}; $\Delta H^{\ddagger}$ = 23.5 kcal mol^{-1}; $\Delta S^{\ddagger}$ = 1 ± 0.5 eu; $\Delta G^{\ddagger}_{30°}$ = 23.1 kcal mol^{-1}. As such, the parameters are comparable to those obtained for the ring opening of the somewhat more stable oxaziridine ring system: $\Delta H^{\ddagger}$ = 28 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −3 ± 1 eu.[24]

The product yields obtained from the ring-opening reactions in the four same solvents are collected in Table IV

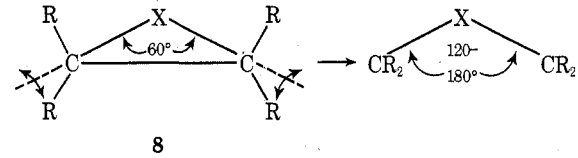
Table IV. Average Product Distributions[a] from Thermal Rearrangements of Oxadiaziridine 5 in Four Solvents

Solvent	Temp, °C	3-(*Z*), %	3-(*E*), %	4-(*Z*), %	4-(*E*), %
CD_3OD	40.5[b]	46	17	22	15
	21.0	45	18	21	15
CD_3CN	40.5	50	15	23	13
	21.0	48	18	20	13
C_6H_6	40.5	47	15	23	15
	21.0	51	15	21	12
CCl_4	40.5	51	16	22	10
	21.0	55	15	21	9

[a] Average of two runs unless otherwise noted; average deviation ±1%. [b] Average of three runs.

and various product ratios which were calculated are presented in Table V. From Table IV it can be seen that as the solvent polarity, as measured by its E_T value, is decreased from CH_3OH to CCl_4 the yield of the least polar product, 3-(*Z*), increases, principally at the expense of the most polar product, 4-(*E*). In Table V two of the ratios listed are of synthetic interest. Since we are able, by N–N bond synthesis, to prepare azoxyalkane 3-(*Z*) in good yield,[19] the oxygen migration effected by thermolysis of oxadiaziridine **5** would extend the utility of that synthesis. In this regard, the most favorable "3/4" ratios are obtained in methanol and, somewhat surprisingly, benzene (at 21°). Regarding the formation of *E* azoxyalkanes, in the event of an unfavorable *Z*–*E* photoequilibrium, thermolysis of the requisite oxadiaziridine can yield an *E* azoxyalkane as was noted previously.[5d] More polar solvents favor the formation of *E* azoxyalkanes as noted previously,[5d] and also as noted by the "*Z*/*E*" ratios of Table V. Again, benzene is seen to behave like a more polar solvent.

In ring-opening reactions of three-membered rings, the steric effects accompanying the rotatory motion of the terminal substituents play an important role in the outcome of such a reaction. Well known are the effects caused by various degrees and orientations of alkyl substitution on the ring-opening reaction of cyclopropyl tosylates and halides[25] (structure 8, X = CH^+). Less well known are the ste-



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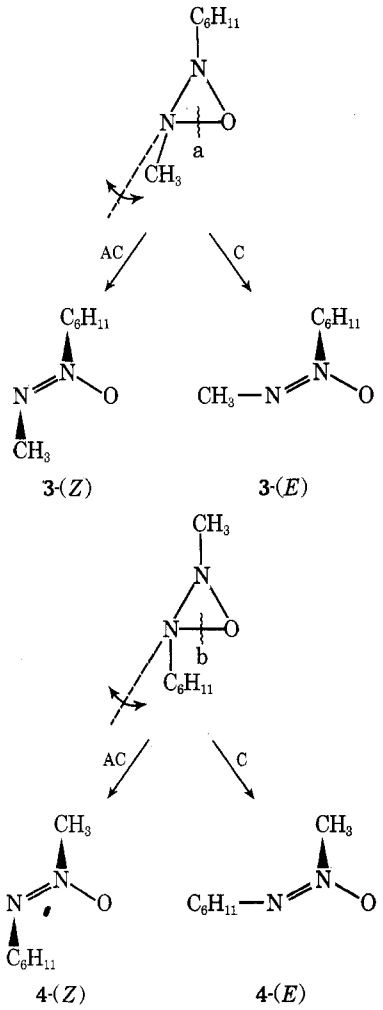
ric influences attending the ring opening of cyclopropylidines (8, X = C:). Thus, with trialkyl substitution on 8 (X = C:), monorotatory ring opening gives allenes as the only reaction products. With tetraalkyl substitution on 8 (X = C:), the ring-opening reaction is completely suppressed (CH insertion occurs), as result attributable to restriction of the rotatory motion of a CR_2 group.[26] Similarly, while substituent electronic effects can influence cyclopropylidine ring opening,[26c,27] the dominant effect is steric in the formation of optically active allenes.[27]

In a similar vein, analysis of the remaining product ratios of Table V indicates that steric effects play a more important role than electronic effects in the ring opening of **5**. Thus, with the aid of Scheme I, the ring opening of **5** can be considered a monorotatory process. Cleavage of N–O bond

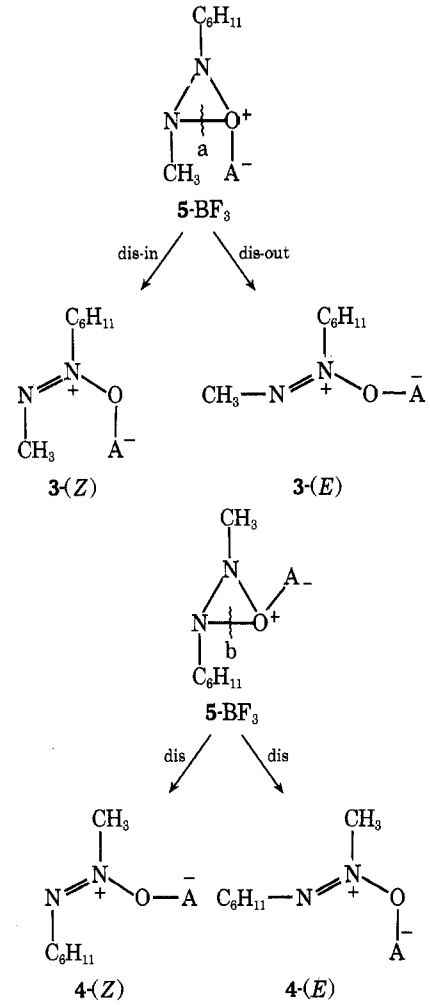
Table V. Product Ratios Obtained from Thermal Rearrangement of Oxadiaziridine 5

Solvent	Temp, °C	3/4	Z/E	3-(Z)/3-(E)	4-(Z)/4-(E)	3-(E)/4-(E)	3-(Z)/4-(Z)
CD_3OD	40.5	1.7	2.1	2.7	1.5	1.1	2.1
	21.0	1.7	2.0	2.5	1.4	1.2	2.1
CD_3CN	40.5	1.8	2.6	3.3	1.8	1.2	2.2
	21.0	2.0	2.2	2.7	1.5	1.4	2.4
C_6H_6	40.5	1.6	2.3	3.1	1.5	1.0	2.0
	21.0	2.0	2.7	3.4	1.7	1.2	2.4
CCl_4	40.5	2.1	2.8	3.2	2.2	1.6	2.3
	21.0	2.3	3.2	3.7	2.3	1.7	2.6

Scheme I



Scheme II[a]



[a] A = BF_3.

a of **5** yields **3** while cleavage of N–O bond b yields products **4**. With cleavage of a, anticlockwise (AC) or clockwise (C) rotation of NCH_3 gives **3**-(*Z*) or **3**-(*E*), respectively. Likewise, with cleavage of b AC rotation of NC_6H_{11} gives **4**-(*Z*), and C rotation gives **4**-(*E*). With bond a cleavage, the rotating CH_3 group "confronts" groups of rather dissimilar size, C_6H_{11} vs. O; in contrast, with bond b cleavage the rotating C_6H_{11} group "confronts" groups of more similar size, CH_3 vs. O. The result is that the **3**-(*Z*)/**3**-(*E*) ratio is always greater than the **4**-(*Z*)/**4**-(*E*) ratio by close to a factor of 2 (CCl_4 solvent excepted).

The data of Table V permit a first estimate of the importance of substituent electronic effects on the ring opening. If we compare the two clockwise ring openings of **5** we see that in both instances, the CH_3 and C_6H_{11} groups confront each other. Thus, the steric effects in these two reactions should be about the same. Examination of the **3**-(*E*)/**4**-(*E*) ratios in Table V indicates a modest preference for the formation of the $C_6H_{11}N(O)$ moiety, wherein the better electron-donating group (Taft σ^* for C_6H_{11} −0.15) is bound to the (formally) positively charged N. By contrast, the relative greater importance of steric effects can be gauged by comparing the two anticlockwise ring openings wherein C_6H_{11} and CH_3 "rotate against" the same group, oxygen. Thus the **3**-(*Z*)/**4**-(*Z*) ratios in Table V exceed 2.

In summary, the relative yields of the four products can be explained principally on the basis of steric effects on the ring opening. Solvent effects alter the percentages of the products but do not change the order: **3**-(*Z*) > **4**-(*Z*) > **3**-(*E*) > **4**-(*E*). Substituent electronic effects may determine the relative yields of the last two compounds.

Acid-Catalyzed Ring Openings of Oxadiaziridines. Both acetic acid and $AgBF_4$ (1 equiv of each) accelerated the ring opening of **2** but did not materially affect the *Z*–*E* ratio of products as measured by NMR spectroscopy. With **5**, 1 equiv of acid was required for efficient catalysis to open the ring, but also, 1 equiv of BF_3 was seen to effect the *E* to *Z* isomerization of **3** and **4**. Thus, the *E* compounds formed by ring opening were isomerized prior to analysis of this reaction and only the **3**-(*Z*)/**4**-(*Z*) ratio was measured. The results are presented in Table VI. A sub-

Table VI. Acid-Catalyzed Ring Opening of Oxadiaziridine 5 in Benzene at 20°

Acid	Molar ratio acid:5	Products[a] 3-(Z), %	4-(Z), %
CH_3CO_2H	1:1	67	33
CH_3CO_2H	4:1	72	28
$BF_3 \cdot OEt_2$	1:1	65	35
$BF_3 \cdot OEt_2$	4:1	49	51

[a] The yields, determined by VPC, represent the sum of E and Z isomers formed in the ring opening.

stantial increase in the more polar products 4 is evident when the ring opening is conducted in the presence of an excess of an acid with bulk sufficient to impart steric effects to its acid–base reactions. It is interesting to note that the increase of 4 is consistent with the intervention of a disrotatory opening of the (probable) preferred conjugate acid of 5. Thus, as Scheme II illustrates, coordination of BF_3 with 5 at oxygen should occur preferentially syn to the less bulky CH_3 group.[28] Cleavage of bond a with dis-in motions of the NCH_3 and O–A groups leads to an unfavorable CH_3–A interaction on the pathway to 3-(Z) congutate acid. Thus, with a restriction placed on the pathway to the major azoxyalkane, 3-(Z), and with no similar restriction placed on the pathway to 4-(Z), the 3/4 ratio, normally 1.7 or greater, could be decreased.[31] Since the azoxyalkanes are recoverable in good yield from these reactions, the acid-catalyzed ring opening of oxadiaziridines holds some synthetic promise for effecting the N to N′ oxygen transfer reaction.

Experimental Section

General. For instruments used, see the Experimental Section of ref 20b. Photochemical reactions were performed in a nitrogen atmosphere using either a medium-pressure 450-W Hanovia type L lamp (lamp H) or a Rayonet photochemical reactor, Model RPR-100 (lamp R) equipped with a 16-tube, variable light source with 350, 300, or 254 nm as the principal emission wavelength choices. Cooling of certain photolysis reactions was accomplished by circulating an externally cooled coolant (usually methanol) around the appropriate immersion well.

VPC columns of aluminum tubing (0.125 and 0.25 in. o.d.) packed with the following adsorbants were used: column A, 5% Carbowax 20M on Anakrom or Chromosorb W (AW and DMCS); B, 5% UCW-98 on Diatoport S; C, 10–20% Carbowax 20M on Chromosorb W (AW and DMCS); D, 20% SE-30 on Anakrom; E, 20% Dow 710 silicone oil on Chromosorb W (AW and DMCS); F, 3 ft × 0.25 in. 20% Dow 710 silicone oil on Chromosorb W (AW and DMCS); G, 10 ft × 0.25 in. 20% SE-30 on Chromosorb W (AW and DMCS).

(Z)-Bis(1-methylethyl)diazene.[32] Thirty-six grams of (E)-bis-(1-methylethyl)diazene[33] was irradiated (lamp R, 350 nm) in a water-cooled Pyrex immersion well for 15–24 h, at which time VPC analysis (column G) indicated 4–7% conversion to the Z isomer. Distillation (760 nm) concentrated the desired Z isomer in the 4-g residue (~40% Z). Repetition of this photolysis–distillation sequence seven times gave 14.8 g of concentrates with 13.8 g of distilled E isomer remaining. Spinning band distillation of the concentrates (60° pot temperature, 80 nm) gave pure E as the distillate and continued distillation with gradual reduction in pressure (to 10 nm) gave 3.94 g of Z isomer (99% purity by VPC analysis, column G): uv λ_{max} 373 nm (ε 103); NMR (CCl_4) δ 1.23 (d, J = 7 Hz, CH_3), 4.05 (septet, J = 7 Hz, CH); the foregoing spectral data were in agreement with literature[32] values.

(E)-Bis(1-methylethyl)diazene Oxide [1-(E)]. A saturated solution of 5.62 g (0.027 mol) of m-chloroperoxybenzoic acid in 30 ml of CH_2Cl_2 was added to a stirred solution of 3.0 g (0.026 mol) of (Z)-bis(1 methylethyl)diazene in 10 ml of CH_2Cl_2 at 0°. After 2 h at 0° the reaction mixture was stirred for 1 h at room temperature, then quenched by the rapid sequential addition of 10 ml of 10% aqueous potassium iodide and 15 ml of 10% aqueous sodium thiosulfate. The organic phase was washed with 20 ml of saturated aqueous sodium bicarbonate, dried (Na_2SO_4), and concentrated in vacuo. NMR analysis of the residue showed the presence of a minor amount of m-chlorobenzoic acid. Column chromatography over 50 g of silica gel using CH_2Cl_2–ether, 10:1 by volume, as eluent and taking 30-ml fractions yielded 2.46 g (72%) of 1-(E) in fractions 5, 6, and 7. Preparative VPC (column E) using the following conditions gave an analytical sample (thermal conductivity detector temperature 150°; column temperature 105°; injection port temperature 150°; carrier gas 200 ml/min): ir (CCl_4) 1480 and 1275 cm^{-1}; uv (EtOH) λ_{max} 232 nm (ε 7900); NMR, see Table II.

Anal. Calcd for $C_6H_{14}N_2O$: C, 55.35; H, 10.84; N, 21.53. Found: C, 55.34; H, 10.83; N, 21.76.

Table VII. Small-Scale Photolysis Results for Compounds 1-(Z) and 1-(E)

Compd (solvent)	Conditions: lamp (nm), filter	Time, hr	Products, % 1-(Z)	1-(E)	2
1-(Z) (neat)	R (350), Pyrex	12	100		
1-(Z) (C_6H_{12})[a]	H, quartz, Vycor	2	94		6
		6	84		16
		16	70		25
1-(Z) ($CHCl_3$)[a]	H, quartz, Vycor	2	96		4
		6	89		11
		9.5	83		17
		16.5	77		22
1-(E) (C_6H_{12})	R (350), Pyrex	16	97	3	
1-(E) (C_5H_{12})[a]	H, quartz, Vycor	2	61	39	
		5	86	7	7
		8	82	2	16

[a] Reaction cooled at 10°.

(E)-2,3-Bis(1-methylethyl)oxadiaziridine (2). A solution of 22 g (0.17 mol) of 1-(Z)[34] in 240 ml of pentane was irradiated (lamp H, Vycor filter) in a water-cooled (10°) quartz immersion well for 17 h. VPC analysis (column E, injection port temperature 80°; temperature program rate 4 min at room temperature, then 8°/min to 120°) indicated the presence of 2 (52%), 1-(Z) (20%), and 28% of other compounds including (E)- and (Z)-bis(1-methylethyl)diazene and 1-(E). A 50-ml aliquot of the mixture was distilled in vacuo (13°, 190 mm) to remove the pentane solvent, and then at 40° (190–25 mm) to yield 1 g of distillate containing equal amounts of 1-(Z) and 2. The distillate was chromatographed over 10 g of silica gel at less than 10° eluting with pentane to give 107 mg of 2 of about 98% purity after distillation of the solvent in vacuo (−20°, 15 mm). An additional 85 mg of 2 was recovered by redistillation of the solvent at −40° (1 mm).

Using a more careful control of temperature and pressure during distillation allowed the isolation of 2 directly from the reaction mixture in 38% yield with purity of about 85%.

Preparative VPC (column F, injection port temperature 80°, column temperature 25°, thermal conductivity detector temperature 85°; carrier gas 200 ml/min) allowed the isolation of pure 2 with less than 1% isomerization to 1-(Z): NMR, see Table II.

Small-Scale Photolyses of 1-(Z) and 1-(E). Solutions containing 50 or 100 mg of 1 at 0.5–1% concentration by volume were irradiated, and the reactions were monitored by VPC analysis (column B, injection port temperature 80°). The results are summarized in Table VII.

Small-Scale Photolyses of 3-(Z) and 4-(Z). Solutions containing 50 to 100 mg of 3-(Z) or 4-(Z) at about 10% concentration by volume were irradiated with lamp H in quartz NMR tubes suspended inside a quartz immersion well which was cooled and fitted with a Vycor filter sleeve. The product ratios were analyzed by NMR spectroscopy (NCH_3 signal integration) and by isolation. The results are summerized in Table VIII.

(E)-Cyclohexylmethyldiazene 1-Oxide [3-(E)]. A solution of 2.5 g of 3-(Z)[19] in 250 ml of pentane was irradiated (lamp H, Vycor filter) in a quartz immersion well at −30° for 2.5 h. The solid which separated was collected by filtration to give 0.77 g (31%) of a mixture of 3-(E) and 4-(E) in a ratio of 12, mp 95–96°. Recrystallization of the solid from benzene–hexane gave 3-(E) of 97% purity [3% 4-(E)]. An analytical sample, mp 98.5°, was obtained by preparative VPC (column D, injection port temperature 135°, column temperature 120°, thermal conductivity detector temperature 125°): ir (KBr) 1500 and 1304 cm^{-1}; uv (EtOH) λ_{max} 232 nm (ε 5900); NMR, Table II.

Anal. Calcd for $C_7H_{14}N_2O$: C, 59.13; H, 9.92. Found: C, 58.92; H, 10.20.

(E)-2-Cyclohexyl-3-methyloxadiaziridine (5). The filtrate from the preceding experiment was concentrated at −30° (2.5

Table VIII. Small-Scale Photolysis Results for Compounds 3-(*Z*) and 4-(*Z*)

Compd (solvent)	Temp, °C	Time, hr	Products, %[a]				
			3-(*Z*)	3-(*E*)	4-(*Z*)	4-(*E*)	5
3-(*Z*) (CD_3OD)	−15	7.5	87	12			Trace
3-(*Z*) (C_5H_{12})	−15	6	93	5[b]			2
4-(*Z*) (CD_3OD)	−25	2.5			98[c]	*c*	2
4-(*Z*) (C_5H_{12})	−25	6			65	31[b]	4

[a] Determined by NMR analysis unless otherwise noted. [b] Isolated yield. [c] In CD_3OD the NCH_3 signals of 4-(*Z*) and 4-(*E*) nearly coincide, making a ratio determination impossible. This experiment predated the knowledge of the utility of the benzene solvent induced shift technique used in the analysis of the rearrangement of 5.

mm), thereby removing the pentane solvent. Further distillation at −20° (0.5 mm) gave 0.68 g (27%) of **5**, NMR ($CDCl_3$) δ 2.60 (s, NCH_3).

The distillation residue, 0.95 g (38%), a mixture of 3-(*Z*) and 4-(*Z*) in a ratio of 6.7, was analyzed by NMR spectroscopy and checked by VPC analysis.

(*E*)-Methylcyclohexyldiazene 1-Oxide [4-(*E*)]. A solution of 3.3 g of 4-(*Z*)[19] in 310 ml of pentane was irradiated (lamp H, Vycor filter) in a quartz immersion well at −30° for 2.5 h. The solid which separated was collected by filtration to give 0.63 g (18%) of nearly pure 4-(*E*), mp 138–140°. Recrystallization from benzene–hexane gave an analytical sample: mp 140–141°; ir ($CHCl_3$) 1500 and 1306 cm^{-1}; uv (EtOH) λ_{max} 233 nm (ε 8000); NMR, Table II.

Anal. Calcd for $C_7H_{14}N_2O$: C, 59,13; H, 9.92. Found: C, 59.39; H, 10.20.

Alternate Preparation of Oxadiaziridine 5. The filtrate from the preceding experiment was concentrated in vacuo at −30° and then chromotographed at −10° over 50 g of silica gel. Elution with 800 ml of 20% CH_2Cl_2 in pentane gave **5** as the first compound off the column. Cold evaporation of the solvent gave 1.89 g (58%) of **5**. Continued elution with 200 ml of CH_2Cl_2 gave 0.44 g (13%) which was principally a mixture of 4-(*Z*) and 3-(*Z*) in a ratio of 1.2. This fraction also contained a small amount of an unknown, presumed to be cyclohexylmethyldiazene as evidenced by a singlet at δ 3.8 in the NMR spectrum of the mixture. (The NCH_3 signal of phenylmethyldiazene occurs at δ 3.9, and that of dimethyldiazene at δ 3.8.)

Thermal Isomerization of 4-(*E*). A solution of 22.0 mg of 4-(*E*) in 0.25 ml of benzene was sealed under nitrogen. The tube was heated in refluxing xylene (138°) and periodically monitored by NMR analysis. At 2 h 40 min, the spectrum had changed from that of 4-(*E*) to that of 4-(*Z*). At 50 min, the NCH_3 signals were approximately of equal intensity.

Thermal Isomerizations of 5. Solutions of 10.0–20.0 μl of **5** in 0.3 ml of solvent were placed in a nitrogen-flushed NMR tube cooled to −80°. To this a known amount (~10 mg) of CH_2Cl_2 was added as internal standard. The initial amount of **5** was estimated by integrating the methyl signal of **5** and CH_2Cl_2. For the rearrangements at 40.5°, the reactions were conducted in the NMR instrument probe and the rate of disappearance of the methyl signal with respect to CH_2Cl_2 was monitored for 3 or 4 half-lives. For rearrangements at the other temperatures, the NMR probe was cooled to the appropriate temperature for the measurements, but the reaction was conducted in a constant-temperature bath. Normally, 8–16 readings were taken in a given experiment and the first-order rate constant obtained by the least-squares method. E_a was calculated, in turn, from the least-squares line of a plot of $1/T$ vs. log k using the eight rate constants obtained in CD_3OD solvent; for $\Delta H^{\ddagger}$ the approximation $\Delta H^{\ddagger} = E_a - RT$ was used (T = 303°); $\Delta S^{\ddagger}$ was calculated from log A (13.6 sec^{-1}). The kinetic data are summarized in Table III. For analysis of product ratios, the sample tube was opened, benzene was added, and the methyl signals reintegrated using the correction noted in the text. When benzene was the solvent, bromobenzene was added to spread the methyl signals of **4**. Periodic VPC analysis of single runs (column A) was used to check the integration results; for example, in CCl_4 (21°) **3/4** = 2.25 by NMR, 2.31 by VPC; in CD_3OD (21°) **3/4** = 1.78 by NMR, 1.91 by VPC; in CD_3CN (21°) **3/4** = 1.88 by NMR, 1.97 by VPC. Product distribution data are collected in Table IV.

Acid-Catalyzed Isomerization of 5. The acid used was added to a cold (15°) solution of ~50 μl of **5** in 1.5 ml of benzene under a nitrogen atmosphere. The density of **5** was assumed to be 1 for purposes of measuring the appropriate molar ratio of acid. After 12 h of stirring at 15–20° the acid was neutralized by the addition of a slight excess of pyridine. (With BF_3, the resulting complex precipitated and was removed by filtration.) A quantitative analysis of the product ratios was made by VPC (column C) under conditions assured to isomerize both *E* isomers. The results are summarized in Table VI. In separate experiments, 1 equiv of boron trifluoride etherate in benzene was seen to effect the isomerization of 3-(*E*) to 3-(*Z*) as evidenced by NMR spectroscopy, and 3-(*Z*) was shown to be stable in the presence of 4 equiv of boron trifluoride etherate as evidenced by VPC analysis (column C).

Registry No.—1-(*Z*), 35216-94-5; 1-(*E*), 35216-96-7; **2**, 57497-44-6; 3-(*Z*), 35214-91-6; 3-(*E*), 35214-90-5; 4-(*Z*), 57497-35-5; 4-(*E*), 57497-45-7; **5**, 57497-46-8; (*Z*)-bis(1-methylethyl)diazene, 23201-84-5; (*E*)-bis(1-methylethyl)diazene, 15464-00-3.

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Crystal and Molecular Structure of Bis(dimethylphosphatovinyl) Carbonate ($C_9H_{16}P_2O_{11}$)

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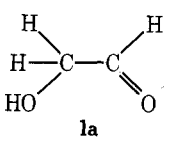
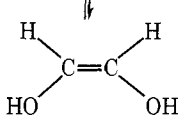
The reaction of 2 mol of 2,2,2-trimethoxy-2,2-dihydro-1,3,2-dioxaphospholene with 1 mol of phosgene ($COCl_2$) gave bis(dimethylphosphatovinyl) carbonate, $C_9H_{16}P_2O_{11}$. The crystal structure of this vinyl phosphate–vinyl carbonate was solved by x-ray diffraction techniques. The crystals grow in an orthorhombic space group *Pbca* with eight molecules per unit cell. The cell dimensions are a = 7.257 (2), b = 21.788 (8), and c = 20.267 (8) Å. Intensities of 1415 reflections were measured on a G.E. XRD-5 diffractometer. The structure was solved by Patterson methods and refined to a final R of 9.5% for 912 observed reflections by least-squares methods. Bond angles around both phosphorus atoms deviate from those of a tetrahedron, ranging from 99.4 to 116.9° and 101.3 to 115.4°, respectively. The formation of a trigonal bipyramidal oxyphosphorane intermediate by the addition of nucleophiles to the phosphorus involves relatively small additional bond angle deformations.

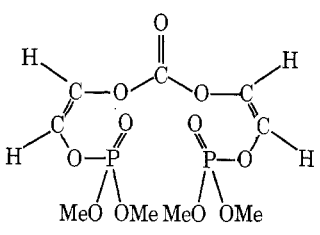
This paper describes the synthesis and the crystal and molecular structure of a carbonate–diphosphate ester, **2**, derived from the enediol tautomer, **1b**, of glycolaldehyde.



1a



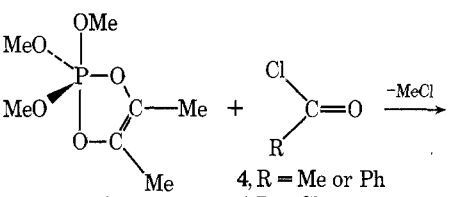
1b



2

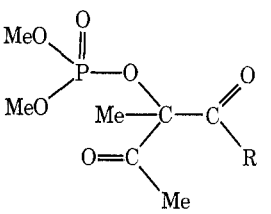
There is now considerable information on the molecular structure and the reactivity of five-membered cyclic unsaturated[2] and saturated[3-7] phosphate esters and phosphate esters of hydroxy ketones.[8,9] The x-ray structure of methyl ethylene phosphate[10] and methyl pinacol phosphate[11] have been described.

Synthesis of Bis(dimethylphosphatovinyl) Carbonate (2). The synthesis of the carbonate **2** is based on a remarkable property of the 2,2,2-trialkoxy-1,3,2-dioxaphospholene system,[12] **3**, with pentacoordinated phosphorus. According to x-ray crystallographic data, the ring in five-membered[13-17] and four-membered[18] cyclic oxyphosphoranes occupies the apical equatorial skeletal position in a trigonal bipyramid. The oxyphosphorane **3** *with two methyl substituents on the ring* undergoes exclusive C-acylation[19] with acyl halides **4** and with phosgene (**5**) under certain conditions, to give phosphate esters of α-hydroxy-β-diketones, **6**, and of α-hydroxy-β-keto acid chlorides, **7**, respectively. In contrast, the oxyphosphorane **8** *with hydrogens on the ring* undergoes exclusive O-acylation[20] under comparable conditions, to give the carboxylate–phosphate



3

4, R = Me or Ph
5, R = Cl



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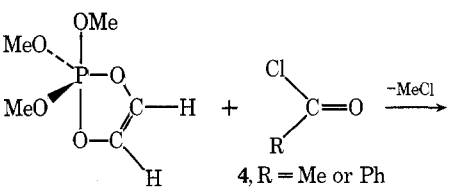

8

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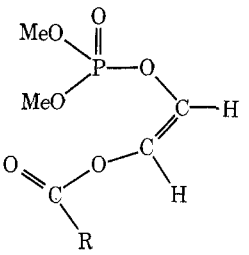
5, R = Cl



9, R = Me or Ph
10, R = Cl