Oxidation of 1,2-Bis(hydroxylamines)

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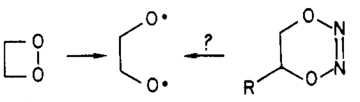
Oxidations of 1,2-bis(aminooxy)ethane ($H_2NOCH_2CH_2ONH_2$) and its phenyl substituted derivative ($H_2NOCHPhCH_2ONH_2$) give a variety of products. Some are consistent with formation of the 1,4,2,3-dioxadiazene ring or a polymeric hyponitrite, while others derive from separate oxidation of the two ends of the hydroxylamine. Nitrogen yields are ~60% in nickel peroxide oxidations and ~25% in *tert*-butyl hypochlorite oxidations.

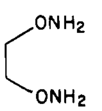
Introduction

The thermolysis of 1,2-dioxetanes, **1**, produces two carbonyl fragments, one of which has enough energy to enter the excited state.[1-5] A number of experiments have lead to the conclusion that the decomposition proceeds via a 1,4-dioxygen diradical, **2**. Many aspects of the mechanism are not yet well understood, however. Among these are the factors which govern the singlet–triplet intersystem crossing of the diradical and the distribution of energy between the two fragments. Other subjects of current interest are the effect of substituents on the activation parameters, the importance of a twisting mode during decomposition, the role of excimers and exciplexes in light production, and the effect of heavy atoms on excited state yield.


1 2 3a, R=H 3b, R=Ph

One approach to understanding the factors involved in excited-state production is to make the intermediate 1,4-dioxygen diradical via a route other than homolytic cleavage of the O–O bond of a dioxetane.[6] A possible precursor to the 1,4-dioxygen diradical is the cyclic hyponitrite, the 1,4,2,3-dioxadiazene **3**. Compound **3** could lose nitrogen to give **2**.

We have attempted to synthesize derivatives of **3** by oxidation of bis(hydroxylamines) **4** and **5**. No dioxadiazenes were in fact seen, although the products of the oxidation were consistent with formation of hyponitrites. The parent chemiluminescent dioxetane (**1** which corresponds to **3a**) has recently been isolated[7a] and is thought to be the intermediate in the gas-phase addition of $^1O_2$ to ethylene, which gives singlet formaldehyde.[7b]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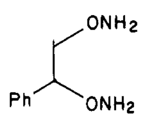
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Results

Synthesis of 1,2-Bis(hydroxylamines). 1,2-Bis(phthalimidooxy)ethane was prepared via the treatment of 1,2-dibromoethane with *N*-hydroxyphthalimide according to a modified procedure of Bauer and Suresh.[8] Hydrazinolysis[9] gave the bis(hydroxylamine) **4**. Attempts to prepare the phenyl-substituted bis(phthalimidooxy)ethane **6** by treating 1,2-dibromo-1-phenylethane[10] in the same way led to elimination, giving phenylacetylene as product.

Phase-transfer catalysis has been used to produce *O*-alkyl-substituted *N*-hydroxyphthalimides[11] and *O*-alkyl-substituted oximes[12] from primary and secondary halides in good yields. However, the reaction of 1,2-dibromoethane with *N*-hydroxyphthalimide or with 1,3-diphenylacetone oxime under phase-transfer conditions (aqueous KOH/Aliquat 336/benzene[13] or aqueous $NaOH/Bu_4N^+Cl^-$/benzene[12a,13a]) gave only low yields of dialkylated products. Attempts to treat 1,2-dibromo-1-phenylethane in a similar way led again to elimination, giving phenylacetylene. Vicinal dibromides have been reported to give alkynes under phase-transfer conditions.[14]

In a third series of experiments, treatment of bromohydrin **7** (ref 15) with diethyl azodicarboxylate (DEAD), *N*-hydroxyphthalimide, and triphenylphosphine[16] gave **8**. Attempted condensation of **8** with *N*-hydroxyphthalimide led only to elimination, giving *N*-[(1-phenylethenyl)oxy]phthalimide, **9**. Compound **5** was successfully prepared by condensation of bromohydrin **10** (ref 17) with 2 equiv of *N*-hydroxyphthalimide in two steps, as shown above, to give **6**, followed by hydrazinolysis of **6** to give **5**.

Oxidation of 1,2-Bis(hydroxylamine) 4. Oxidation of 1,2-bis(aminooxy)ethane, **4**, with *tert*-butyl hypochlorite at −78 °C gave ethylene glycol and compound **12**, in ad-

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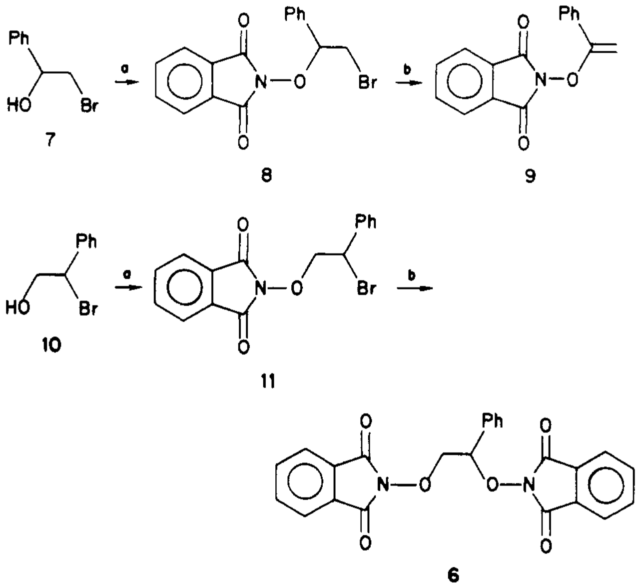
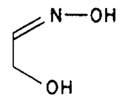


(a) *N*-Hydroxyphthalimide, DEAD, Ph_3P, THF, room temperature; (b) *N*-hydroxyphthalimide, Et_3N, DMF, room temperature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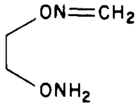
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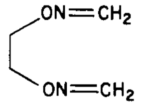
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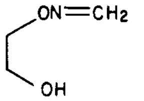
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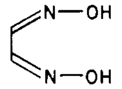
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dition to recovered 4, in approximately 15% total yield as determined by comparison with authentic samples. Evolution of a gas was detected. No formaldehyde condensation products were identified. In particular, none of the possible condensation products **13–15** nor bis(oxime) **16** were products of the oxidation.

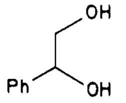
Oxidation of 4 at −78 °C with nickel peroxide[18] gave ethylene glycol and **12**, while oxidation with nickel peroxide alone gave only ethylene glycol. Yields were about 10%. Evolution of a gas was detected. Attempts to detect free formaldehyde by the method of Nash[19] were unsuccessful. Formaldehyde is very reactive, however, and it may have polymerized in the organic solvent. This would explain the low yield of isolated products, as well as the observation that the yield of nitrogen evolved from the reaction (61%, see below) was much higher than the yield of other products.

The bis(hydroxylamine) 4 was also oxidized with Ag_2CO_3 on Celite,[20] Na_2WO_4/H_2O_2,[21] *tert*-butyl hypochlorite/DABCO,[22] PbO_2,[23] and Br_2/Na_2CO_3.[24] In all cases, the major product seen by NMR was ethylene glycol.

Table I. Nitrogen Yields in the Oxidation of 1,2-Bis(hydroxylamines)

compd	oxidant	% yield of nitrogen
4	$(CH_3)_3COCl$	21
4	nickel peroxide	61
5	$(CH_3)_3COCl$	29
5	nickel peroxide	63

Oxidation of 1,2-Bis(hydroxylamine) 5. Oxidation of 1-phenyl-1,2-bis(aminooxy)ethane, **5**, with *tert*-butyl hypochlorite at −78 °C gave 13 compounds. Evolution of a gas was also evident. The structures of ten of the compounds (benzaldehyde, benzoic acid, and **17–24**) were assigned in accord with the mass spectra taken on the silylated reaction mixture. Details of the assignments are given in the Supplementary Material. Product recovery was approximately 65% by GC relative to an internal standard. The yield of each compound was less than 10%.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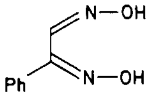
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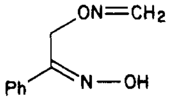
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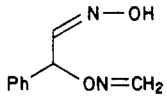
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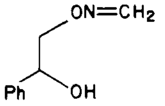
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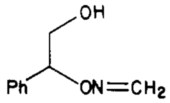
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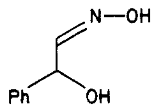
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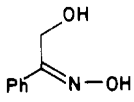
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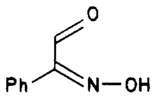
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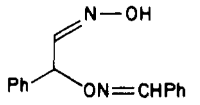
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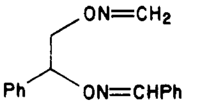
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The presence of benzaldehyde and of formaldehyde condensation products **19–22** are consistent with a hyponitrite (either **3b** or a polymer) as an intermediate. The hyponitrite could decompose to benzaldehyde formaldehyde, and nitrogen. The benzaldehyde and formaldehyde could then react with any hydroxylamine present. The benzaldehyde does not come from oxidation of 1-phenyl-1,2-ethanediol, **17**, as **17** is stable to the oxidation conditions. From the product distribution, it appears that approximately one-third of **5** oxidizes to a hyponitrite, one-third reacts with decomposition products of the hyponitrite, and one-third rearranges to other products.

Oxidation of **5** with nickel peroxide at room temperature gave benzaldehyde, benzoic acid, and compounds **17**, **19–22** and **25–27**. Two additional compounds were unidentified. Evolution of a gas was detected. Compound **25** comes from oxidation of **24**. Compound **26** is a benzaldehyde condensation product while **27** contains both benzaldehyde and formaldehyde.[25]

Evolution of Nitrogen. Oxidation of either of the 1,2-bis(hydroxylamines) with nickel peroxide or *tert*-butyl hypochlorite produced gaseous nitrogen. The amount was determined by GC. Table I shows that the nickel peroxide oxidation gave a much higher yield of nitrogen than did the *tert*-butyl hypochlorite oxidation. In the nickel peroxide oxidation of either of the 1,2-bis(hydroxylamines), the nitrogen was completely evolved in less than 5 min at room temperature indicating that the primary oxidation products were unstable.

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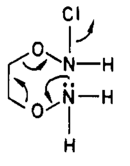
Detection of substantial amounts of nitrogen may indicate that the oxidation proceeds to give cyclic hyponitrites, although acyclic monomers or acyclic polymers are also possibilities. Formation of an N–N bond in the oxidation of a 1,4-diamine depends on both substrate and oxidant. Syntheses of cyclic hydrazines,[26,27] diazenes,[21,28] tetrazenes,[29,30] and dicarbalkoxy-1,4,2,3-dioxadiazines[31] have been effected by oxidation of the corresponding diamines. Yields vary from <5 to ~60%.

Ethylene. Oxidation of 1,2-bis(hydroxylamines) might also have resulted in the formation of ethylene via a Grob-type[32] fragmentation **29**. No ethylene was detected in the oxidation of 4 with *tert*-butyl hypochlorite and triethylamine, showing that this fragmentation was not an important pathway.



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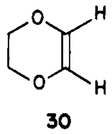

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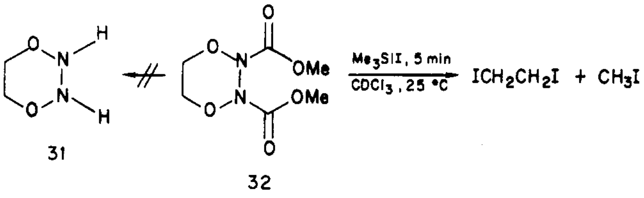
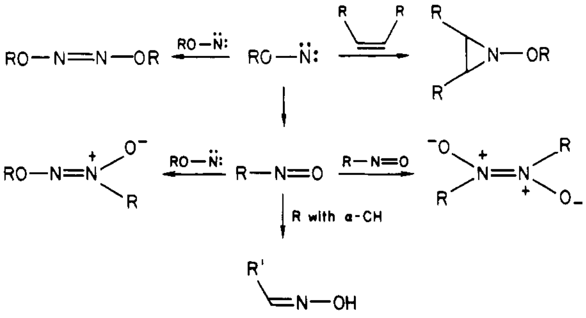
Attempted Spectral Observation. A number of attempts were made to see intermediates in the oxidation of 4 by ^{1}H NMR (100 and 360 MHz) at low temperature. In no case was a resonance seen that changed with time or temperature. It is expected that the methylene protons of **3a** would be a singlet at about 4 ppm. The temperature dependence of the ^{1}H NMR spectrum of 1,4-dioxene, **30**, has been measured from −150 °C to room temperature in vinyl chloride.[33] The methylene protons remained a fairly sharp singlet even at −116 °C ($\nu_{1/2}$ ~3 Hz). Splitting did not occur until about −129 °C. Therefore we expect that the dioxadiazene ^{1}H NMR spectrum would probably also be a singlet even at −78 °C.

Chemiluminescence. When bis(hydroxylamine) **5** was oxidized with *tert*-butyl hypochlorite (either with or without triethylamine) in the presence of the added fluorescers 9,10-dibromoanthracene or 9,10-diphenylanthracene,[34] no light emission was detected by the dark-adapted eye. Similar results were obtained in the *tert*-butyl hypochlorite oxidation of **4** and in the nickel peroxide oxidation of either **4** or **5**.

Attempted Preparation of 3a from a Dioxadiazine. A second route to the cyclic hyponitrite, from the dioxadiazine ring **31**, was also attempted. Alkyl carbamates can be converted to *O*-trimethylsilyl carbamates with iodotrimethylsilane.[35] The trimethylsilyl groups can be removed in turn with either alcohols or fluoride ion and the resulting R_2NCO_2H moiety loses CO_2 easily.[35]



Scheme I



Treatment of **32** (ref 31) with iodotrimethylsilane resulted in complete destruction of the ring. Methyl iodide and 1,2-diiodoethane were found. Detection of 1,2-diiodoethane implies attack at the ring carbons as well as at the methoxy carbon. A control experiment in which iodotrimethylsilane was added to dioxane showed no decomposition of the dioxane after 15 h at room temperature (NMR, $CDCl_3$).

The literature on iodotrimethylsilane indicates that benzyl groups[35,36] are cleaved 60- to 100-fold more quickly than methyl groups. Attempts to make the dibenzyl ester of the dioxadiazine were thwarted when addition of benzyl chloroformate to **4** gave mixtures of products rather than the 1,2-bis(urethane).

Discussion

Oxidation of Hydroxylamines. *trans*-Hyponitrites are usually synthesized from the condensation of alkyl halides and *trans*-$Ag_2N_2O_2$.[37,38] Although it is possible to use hyponitrites with counterions other than Ag[37] and *cis*-$Na_2N_2O_2$ is known,[39] the condensation of *cis*-$Na_2N_2O_2$ with 1,2-dihalides would probably lead in part to explosive hyponitrite polymers. We therefore chose an alternate route, the oxidation of a bis(hydroxylamine). It has been reported that oxidation of *tert*-butylhydroxylamine with bromine and base leads to the *trans*-hyponitrite.[24]

In general, oxidation of hydroxylamines gives products which can be viewed formally as resulting from the alkoxynitrene,[40–43] although it is, in fact, unlikely that the free nitrene is the intermediate in most cases.[44,45] The product

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Table II. Activation Parameters for Diazene Decomposition

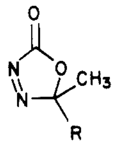
compd	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal deg^{-1}	k (100 °C)^{a} s^{-1}	ref
34	42.1	16.3	6.1×10^{-9}	53
35	36.6	11.8	1.1×10^{-6}	54
36	36.1	4.7	5.8×10^{-8}	29, 55
37	38	17	2.2×10^{-6}	29
28	27.9	8.2	2.2×10^{-2}	38

[a] Calculated from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

mixtures (Scheme I) are heavily dependent on substituent, solvent, oxidant, and temperature, with alcohols[43-48] (probably from hyponitrite decomposition), nitroso compounds,[42,47,48] and oximes[41,44,47] (from rearrangement of the nitroso compound) predominating.

As discussed above, oxidation of the 1,2-bis(hydroxylamines) leads to a variety of products consistent with those in Scheme I. In the oxidation of **5**, many aldehyde condensation products were observed; oxidation of the unsubstituted **4** showed no condensation products. This may reflect the production of two molecules of formaldehyde in proximity from the oxidation of **4**; oxidation of **5** gives 1 equiv each of formaldehyde and benzaldehyde.

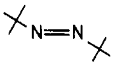
Alternately, it may represent more facile decomposition of the oxidation products of **5** than those of **4**. If the products of **5** decompose at a lower temperature, polymerization of the formaldehyde would be suppressed. If the products are the cyclic hyponitrites and decomposition occurs through a 1,4-dioxygen diradical,[49] the phenyl group should not have a large effect on the rate because decomposition of hyponitrites is not heavily dependent on substituent.[50] A concerted decomposition of cyclic hyponitrite **3b** should show a moderate rate enhancement by the phenyl group. Paine and Warkentin[51] have studied the decomposition of Δ^3-1,3,4-oxadiazolin-2-ones **33**. The reaction is thought to be concerted, and phenyl-substituted **33a** decomposes 170 times faster than methyl-substituted **33b**.



33a, R = Ph
33b, R = CH$_3$

A third possibility for the difference in products in the oxidation of **4** and **5** is that ring closure of **5** to the dioxadiazene could be more facile than that of **4** because the phenyl group of the former would favor conformations of **5** appropriate for ring closure. Related effects have been observed in other systems.[52]

Estimate of the Thermal Stability of 3a. The cyclic *cis*-hyponitrite is expected to be unstable. However, if the first step in the decomposition is loss of nitrogen to give the dioxygen diradical **2**, then the half-lives of *cis*- and *trans*-diazenes and *cis*- and *trans*-tetrazenes indicates that **3a** should be stable at least for short periods of time at room temperature. Activation parameters and calculated rates of decomposition for diazenes at 100 °C are shown in Table II. The cyclic diazene **35** (ref 54) decomposes 180 times faster than the acyclic diazene **34** (ref 53); the cyclic tetrazene **37** (ref 29) decomposes about 40 times faster than its acyclic counterpart **36** (ref 55). If one assumes that the dioxadiazene **3a** decomposes 40–180 times faster than di-*tert*-butyl hyponitrite, **28** (ref 38), then $\tau_{1/2}$ = 0.2–1 s at 100 °C. Even if the dioxadiazene were to decompose 1000 times faster than *trans*-hyponitrite, it should have a $\tau_{1/2}$ of ~12 h at 0 °C. It should be noted that *cis*-dialkyldiazenes are generally 5–8 kcal mol^{-1} less stable than their trans isomers,[53b] but that replacement of alkyl groups by more electronegative substituents reduces this difference and may even favor the cis form slightly.[56] The comparisons above assume that all fragmentations involve initial loss of nitrogen. If the decomposition of **3a** is a concerted three-bond fragmentation then the rate may be much faster than these calculations indicate.



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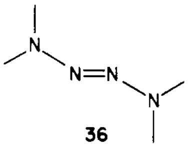

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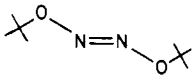

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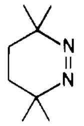

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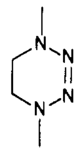

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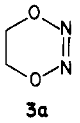

3a

Efforts to observe **3a** by NMR were unsuccessful. It is possible that **3a** is very unstable or that it undergoes decomposition under the conditions of the reaction. Alternately, if the methylene hydrogens of **3a** are a multiplet rather than a singlet, it may be difficult to distinguish **3a** from the other products. As discussed above, the observation that dioxene **30** is a singlet down to −116 °C[33] makes this unlikely. Finally **4** may oxidize to a polymer rather than a monomer. Hyponitrite dimers and trimers would have more complicated spectra, but moderate length chains would be expected to appear as a singlet in the NMR also.

Energetics. Group additivity heats of formation are not available for the hyponitrite linkage, but it can be estimated that the decomposition of **3a** to two molecules of formaldehyde and nitrogen has a $\Delta H° \simeq -70$ kcal mol^{-1} (ref 57). If the activation energy for decomposition is ~20 kcal mol^{-1}, the overall exothermicity is ~90 kcal mol^{-1}. This is similar to that in the dioxetane system.[1-5] Decomposition of a dioxadiazene should have enough energy

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(57) Group additivity estimates are taken from Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976. $\Delta H°_f$ (**3a**) $\simeq$ 2[C–(H$_2$)(O)(C)] + 2[O–(C)(N$_A$)] + 2[N$_A$–(O)] $\simeq$ 2(−8.1) + 2[O–(C)(NO)] + 2[N$_A$–(N)] $\simeq$ −16.2 + 2(−5.9) + 2(23) $\simeq$ 18 kcal. For the decomposition $\Delta H° = \Delta H°_f$ (N$_2$) + $2\Delta H°_f$ (H$_2$CO) − ΔH_f (**3a**) = 0 + 2(−26.0) − 18 = −70 kcal. The energy available to form excited state products is $\Delta H° + \Delta H^{\ddagger}$.

to populate the excited singlet or triplet of formaldehyde (83.6 and 72.2 kcal mol^{-1})[58] or those of benzaldehyde (77.1 and 72.0 kcal mol^{-1}).[59]

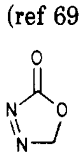
The 1,4-dioxygen diradical, **2**, might close to the dioxetane, **1**, as well as cleave to two aldehydes. In the decomposition of dioxetanes, it is not known experimentally whether any of the initially formed diradical recloses. Thermochemical calculations of Richardson and O'Neal[60] have indicated that the closure and cleavage pathways have activation energies of 8.5 and 6.5 kcal mol^{-1}, respectively. Ab initio GVB calculations of Harding and Goddard[61] have put the barrier of cleavage slightly higher than that of ring closure. The cleavage barrier cannot be substantially higher than that of ring closure or experiments designed to detect changes in the C–C bond at the transition state (substituent and isotope studies) would have detected C–C bond weakening or breaking. We have not detected any dioxetanes in our reactions. If they formed, they may have undergone decomposition catalyzed by the reactants. Amines and transition metals are known to catalyze dioxetane decomposition.[1,2]

Mechanism of Decomposition. Fragmentations may be classed in terms of the number of bonds broken and the number of resulting fragments. For example, the reverse Diels–Alder and cyclobutane to ethylene conversions are two-bond, two-fragment (2B2F) decompositions.

Decomposition of a 1,4,2,3-dioxadiazene might proceed via an initial one-bond (1B1F), two-bond (2B2F), or three-bond (3B3F) cleavage. A one-bond cleavage would lead to the prediction that the dioxadiazene would be quite stable. Casewit and Goddard[56] have calculated that the reaction $ArN{=}N{-}OCH_3 \rightarrow ArN_2\cdot + \cdot OCH_3$ is endothermic by 33 kcal mol^{-1}. A two-bond cleavage would result in the 1,4-dioxygen diradical, **2**, which would cleave to two aldehydes. As discussed above, the decomposition is sufficiently energetic to form one of the aldehydes in its excited state. Acyclic *trans*-hyponitrites decompose via a two-bond pathway.[49] A three-bond, or concerted, fragmentation would follow $\sigma 2s + \sigma 2s + \sigma 2s$ stereochemistry and produce all three fragments in their ground states.

However, although this 3B3F fragmentation is allowed, it is not necessarily the lowest energy pathway. Many molecules do not take advantage of the kinetic benefit of concert when that concert would involve simultaneous cleavage of three bonds. Lai and Tidwell have reviewed the literature on one-bond vs. two-bond vs. three-bond cleavage for acyclic systems.[62] The corresponding literature for cyclic systems is summarized below.

3B3F decompositions, while formally allowed, are rare. Of the systems studied in this context, there is strong evidence for a 3B3F decomposition in **33** (ref 51) and **38** (ref 63a). Ring systems **39** (ref 63b) and **40** (ref 64) are also thought to follow this pathway. Other systems such as **41** (ref 65), **42** (ref 66), **43** (ref 67), **44** (ref 68), and **45** (ref 69) do not undergo a 3B3F decomposition.[70]



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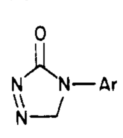

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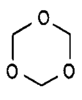

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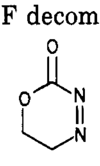

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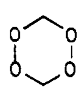

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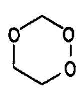

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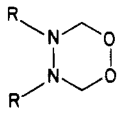

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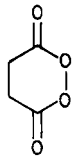

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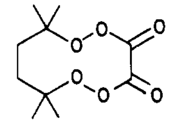

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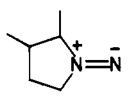

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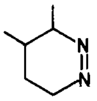

47

The 1,1-diazenes **46** and 1,2-diazenes **47** apparently follow both 2B2F and 3B3F pathways. For example, analysis of the products from the decomposition of *cis*-**46** indicated 38% of a direct cleavage pathway and 62% of a biradical pathway; *trans*-**46** underwent 51% direct and 49% biradical cleavage.[71a] Similar analyses of the 1,2-diazene decomposition products indicated 36% direct/64% 1,4-biradical from *cis*-**47** and 32% direct/68% 1,4-biradical from *trans*-**47** (ref 71b).

Other instances of reactions following a diradical pathway when a concerted one is available are also known. Turro et al. have studied anthracene *endo*-peroxides.[72] Activation enthalpies, singlet oxygen yields, oxygen isotope effects, and magnetic field effects on product ratios indicated that the 1,4-*endo*-peroxides decomposed concertedly but that the 9,10-*endo*-peroxides decomposed primarily by a radical route involving cleavage of the O–C bond. The above discussion indicates that the 3B3F $\sigma 2s + \sigma 2S + \sigma 2s$ route, though allowed by orbital symmetry, need not be the route of the decomposition.

Conclusion

Oxidation of 1,2-bis(hydroxylamines) **4** and **5** gives a variety of products. Some derive from separate oxidation of the two ends of the hydroxylamine; others are consistent with formation of a hyponitrite. Nitrogen yields are ~25% in the *tert*-butyl hypochlorite oxidation and ~60% in the nickel peroxide oxidation. Although the cyclic hyponitrite **3** is estimated to have a half-life of hours at 0 °C, it was not observed, either because the intermediate was a polymeric hyponitrite or because **3** is less stable than predicted on the basis that the initial step is a 2B2F loss of nitrogen.

Experimental Section

General Methods. ^{1}H NMR were obtained on a 60-MHz Hitachi Perkin-Elmer R-24B spectrometer. Low-temperature ^{1}H NMR studies were done on a JEOL FX-100 spectrometer. ^{1}H and ^{13}C NMR spectra are reported in parts per million (δ) relative

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to Me_4Si (δ 0.0). Infrared spectra were taken on a Perkin-Elmer 283B spectrophotometer. ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer. Mass spectra were obtained on a Finnegan 3200 GC/MS using a 4 ft × $^1/_4$ in. 3% OV-17 column. Gas chromatography was done on a Hewlett-Packard 5750 research chromatograph using a 5 ft × $^1/_8$ in. 10% OV-17 on 80/100 mesh Chromosorb column (column A) or a 6 ft × $^1/_8$ in. 5Å molecular sieves 60–80 mesh column (column B).

Melting points (mp) were determined using a Thomas Hoover Uni-Melt apparatus and are corrected.. Boiling points (bp) are uncorrected. *tert*-Butyl hypochlorite was purchased from Frinton and purified by vacuum distillation. Diethyl azodicarboxylate (DEAD), *N*-hydroxyphthalimide, glycolaldehyde, iodotrimethylsilane, and *N*-(trimethylsilyl)imidazole were purchased from Aldrich and were used as received. For the DEAD-mediated condensations the *N*-hydroxyphthalimide and Ph_3P were dried overnight under vacuum. Hydrazine was purchased from J.T. Baker Chemical Co. Glyoxime (**16**) was purchased from Eastman.

1,2-Bis(phthalimidooxy)ethane was prepared according to a modified procedure of Bauer and Suresh[8] in which 1 equiv of 1,2-dibromoethane was alkylated with 2 equiv *N*-hydroxyphthalimide in dimethylformamide containing 6 equiv of triethylamine to give an 84% yield of the desired product as white needles. The solid could be recrystallized from hot dimethylformamide but was usually used without further purification: mp 248–249 °C (lit.[8] mp 254 °C).

1,2-Bis(aminooxy)ethane (4). Hydrazine (95%, 5.81 mL, 0.174 mol) was added dropwise via syringe over a 10-min period to a stirred suspension of 1,2-bis(phthalimidooxy)ethane (20.0g, 0.0568 mol) in 95% EtOH (120 mL) at room temperature under N_2. The reaction was mildly exothermic and 5 min after addition was complete phthalhydrazide precipitated from the solution. The white precipitate was broken up with a spatula and the mixture was stirred for 2 h. Additional 95% EtOH (50 mL) was added, the mixture was filtered, and the collected phthalhydrazide was washed with 95% EtOH. The filtrates were combined and the solvent was removed under reduced pressure. CH_2Cl_2 (100 mL) was added to the residue and the solution was stored at 10 °C overnight to precipitate dissolved phthalhydrazide. The solution was filtered, dried ($MgSO_4$), and the solvent was removed under reduced pressure to give 3.39 g of a colorless liquid (65% yield): IR ($CHCl_3$) 3325, 3000, 2925, 1585, 1188, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.71 (s, 4 H), 5.31 (br s, 4 H, exchanged with D_2O); ^{13}C NMR ($CDCl_3$) δ 73.7; mass spectrum, m/e (relative intensity) 93 (M^+ + H, 100), 92 (M^+, 20), 66 (59), 65 (23), 64 (10), 63 (13).

The compound had been previously characterized as its dihydrobromide salt.[8]

1-Phenyl-1,2-bis(aminooxy)ethane (5) was prepared as a yellow liquid (96% yield) from **6** following the procedure for the preparation of **4**. The yellow liquid solidified during storage at −10 °C for 24 h: mp 25 °C; IR ($CHCl_3$) 3325, 3000, 1583, 1454, 1184, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.88 (m, 2 H), 4.94 (m, 1 H), 5.32 (br s, 4 H, exchanged with D_2O), 7.42 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 138.5, 128.6, 128.1, 126.9, 85.0, 78.4; mass spectrum, *m/e* (relative intensity) 136 ($M^+ - ONH_2$, 49), 121 (14), 105 (58), 104 (49), 103 (25), 92 (24), 91 (100), 79 (25), 78 (31), 77 (77), 51 (40).

Compound **5** was also characterized as its dihydrochloride salt. HCl gas was bubbled for 30 min through a stirred solution of **5** (304 mg, 1.87 mmol) in ether (50 mL) at room temperature. The precipitated white solid was filtered, washed with ether, and recrystallized from MeOH/ether to give 344 mg of white crystals (78% yield): mp 163.0–163.5 °C; IR (KBr) 2890, 2660, 1920, 1490, 1027, 767 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 4.41 (d, 2 H), 5.65 (t, 1 H), 7.46 (s, 5 H), 11.15 (br s, 6 H); ^{13}C NMR (Me_2SO-d_6) δ 133.6, 129.4, 128.7, 127.3, 82.1, 74.4; mass spectrum, *m/e* (relative intensity) 136 (M^+ − 2HCl, ONH_2, 63), 106 (26), 105 (74), 104 (55), 92 (27), 91 (100), 79 (28), 78 (29), 77 (80), 51 (37). Anal. Calcd for $C_8H_{14}Cl_2N_2O_2$: C, 39.85; H, 5.85; N, 11.62. Found: C, 39.88; H, 5.89; N, 11.79.

1-Phenyl-1,2-bis(phthalimidooxy)ethane (6). A red mixture of *N*-hydroxyphthalimide (6.55 g, 0.0401 mol), **11** (13.9 g, 0.0401 mol, contained in residue A), and triethylamine (33.5 mL, 0.240 mol) in DMF (125 mL) was allowed to sit at room temperature for 4 days. The mixture was filtered to remove precipitated triethylammonium bromide and the solvent was removed under reduced pressure to give a red gummy solid. Methanol (150 mL) was added and the mixture was warmed (40 °C). A white solid formed after about 30 min of warming, swirling, and scratching the red gum. The solid was collected by filtration and was purified by boiling in MeOH (to remove any **11**) to give 11.6 g of a white solid (67% yield, >95% pure).

An analytically pure sample was obtained by preparative TLC on a 1000 μm Analtech silica gel GF plate developed with $CHCl_3$. The band with R_f 0.18 was scraped off and eluted with $CHCl_3$. The $CHCl_3$ solution was filtered and dried ($MgSO_4$). The $CHCl_3$ was removed under reduced pressure to give a white solid that was boiled in MeOH to give analytically pure compound: mp 194.0–194.5 °C; IR ($CHCl_3$) 1796, 1740, 1376, 882, 701 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 4.73 (m, 2 H), 5.72 (m, 1 H), 7.44 (m, 5 H), 7.83 (s, 8 H); ^{13}C NMR (Me_2SO-d_6) δ 163.1, 162.8, 134.6, 134.4, 129.3, 128.5, 128.3, 123.2, 85.2, 78.4; mass spectrum, *m/e* (relative intensity) 266 ($M^+ - C_8H_4NO_3$, 3.4), 147 (10), 119 (31), 104 (35), 91 (100), 79 (79), 77 (28), 76 (34), 52 (62), 51 (38), 50 (33). Anal. Calcd for $C_{24}H_{16}N_2O_6$: C, 67.29; H, 3.76; N, 6.54. Found: C, 67.03; H, 3.65; N, 6.47.

2-Bromo-1-phenylethanol (7) was prepared in 54% yield as a colorless oil according to the procedure of Guss and Rosenthal.[15] The ^1H NMR spectrum of the oil matched the literature spectrum:[73] bp 98–100 °C (1 mm) [lit.[15] bp 120–123 °C (5 mm)].

***N*-(2-Bromo-1-phenylethoxy)phthalimide (8).** A solution of diethyl azodicarboxylate (DEAD) (2.6 mL, 16 mmol) in anhydrous THF (5 mL) was added dropwise over a 15-min period to a stirred mixture of *N*-hydroxyphthalimide (2.46 g, 15.0 mmol), 2-bromo-1-phenylethanol (2.61 g, 13.0 mmol), and finely powdered triphenylphosphine (3.93 g, 15.0 mmol) in THF (25 mL) at room temperature under N_2 in a flame-dried apparatus. The mixture turned red upon addition of DEAD and then yellow after stirring for 15 min. The mixture was stirred for a total of 12 h. The solvent was removed under reduced pressure to give 12.5 g of a yellow slurry of solid and liquid. Part of the slurry (2.80 g) was chromatographed on silica gel (70–230 mesh, Merck) using $CHCl_3$ as eluant. The aliquots containing **8** (R_f 0.57 on silica $CHCl_3$) were combined and dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a white solid. The solid was recrystallized from benzene/hexane to give 690 mg (69% yield) of **8** as colorless needles: mp 133.5–134.0 °C; IR (KBr) 2965, 1790, 1725, 1359, 978, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.81 (apparent dd, 2 H), 5.55 (t, 1 H), 7.39 (m, 5 H), 7.70 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 163.5, 135.2, 134.5, 129.8, 128.7, 128.6, 128.1, 123.5, 87.9, 31.4; mass spectrum, *m/e* (relative intensity) 265 (M^+ − HBr, 28), 185 (100), 183 (100), 105 (46), 104 (97), 103 (72), 78 (44), 77 (69), 76 (83), 51 (44), 50 (48). Anal. Calcd for $C_{16}H_{12}BrNO_3$: C, 55.51; H, 3.49; N, 4.04. Found: C, 55.33; H, 3.38; N, 3.99.

2-Bromo-2-phenylethanol (10) was prepared in 93% yield as a clear oil according to the procedure of Stille and Cowell.[17] ^1H NMR and IR spectra of the oil matched literature spectra.[17] Large scale purification (100 g) was achieved by passing a $CHCl_3$ solution of the oil through a bed of silica gel.

***N*-(2-Bromo-2-phenylethoxy)phthalimide (11).** A solution of diethyl azodicarboxylate (DEAD) (27.9 mL, 0.177 mol) in anhydrous THF (50 mL) was added dropwise over a 3-h period to a stirred mixture of *N*-hydroxyphthalimide (26.3 g, 0.161 mol), 2-bromo-2-phenylethanol (49.8 g, 0.248 mol), and finely powdered triphenylphosphine (42.2 g, 0.161 mol) in THF (130 mL) at 0 °C under N_2 in a flame-dried apparatus. The mixture turned red upon addition of DEAD but changed to yellow by the time addition was complete. The mixture was stirred for 30 min at 0 °C and then for 18 h at room temperature. The solvent was removed under reduced pressure to give 150 g of a brown viscous liquid (residue A). Chromatography (see below) and ^1H NMR showed that residue A contained **11** (25% yield, estimated by NMR) and its rearranged isomer **8** (27% yield). The identity of **8** was confirmed by comparison with an authentic sample. Residue A could be purified by chromatography but was usually used directly in the preparation of **6**.

In a typical chromatographic purification, a portion of residue A (4.38 g) was dissolved in a minimum amount of $CHCl_3$ and chromatographed on a silica gel column (70–230 mesh, Merck)

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(73) Ziffer, H.; Kawai, K.-i.; Imuta, M. *J. Org. Chem.* **1980**, *45*, 3352–3355.

using $CHCl_3$ as eluant. The aliquots containing product (R_f 0.69, silica, $CHCl_3$) were combined and dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a white solid (1.08 g) that was recrystallized from MeOH. The solid was a mixture containing equal amounts of **11** and **8** (by NMR). Separation of up to 50 g of residue A in a column containing 1 kg of silica gel was achieved: mp of mixture 100–101 °C; IR of mixture ($CHCl_3$) 1790, 1738 cm^{-1}; ^1H NMR of **11** ($CDCl_3$) δ 4.69 (m, 2 H), 5.29 (m, 1 H), 7.35 (m, 5 H), 7.69 (s, 4 H); ^{13}C NMR of **11** ($CDCl_3$) δ 80.3, 48.1 (other peaks not assigned); mass spectrum of mixture, *m/e* (relative intensity) 265 (M^+ – HBr, 0.16), 183 (16), 104 (100), 91 (15), 79 (46), 78 (34), 77 (29), 76 (39), 52 (33), 51 (30), 50 (30). Anal. Calcd for $C_{16}H_{12}BrNO_3$ isomers: C, 55.51; H, 3.49; N, 4.04. Found: C, 55.33; H, 3.46; N, 4.04.

Nickel peroxide was prepared as a black solid according to the procedure of Nakagawa, Konaka, and Nakata.[18a] The available oxygen content was in the range 1.03–1.10 mol of O per gram Konaka, and peroxide as determined by iodometric titration.[18a]

Oxidation of 1,2-Bis(aminooxy)ethane (4). The products from all the oxidation were analyzed by GC/MS as described in the supplementary material.

With *tert*-butyl hypochlorite: *tert*-butyl hypochlorite (0.49 mL, 4.3 mmol) was added via syringe to a stirred solution of **4** (200 mg, 2.17 mmol) in CH_2Cl_2 (5 mL) at –78 °C under N_2. Evolution of a gas was detected. The resulting yellow mixture was stirred for 2 h at –78 °C and was then filtered at –78 °C.

With nickel peroxide and triethylamine: nickel peroxide (8.05 g, 8.86 mol of O) was added neat to a stirred solution of **4** (200 mg, 2.17 mmol) and triethylamine (0.61 mL, 4.4 mmol) in ether (10 mL) at –78 °C under N_2. Evolution of a gas was detected. The mixture was stirred for 2 h at –78 °C and was then filtered at –78 °C.

With nickel peroxide: the procedure was the same as above except that triethylamine was omitted. The only product was ethylene glycol in about 10% yield. Evolution of a gas was detected.

Oxidation of 1-Phenyl-1,2-bis(aminooxy)ethane (5). With *tert*-butyl hypochlorite: the procedure was the same as that for the oxidation of **4**. Evolution of a gas was observed.

With nickel peroxide and triethylamine: nickel peroxide (3.47 g, 3.57 mol of O) was added to a stirred solution of **5** (100 mg, 0.595 mmol) and triethylamine (82 μL, 0.59 mmol) in CH_2Cl_2 (25 mL) at room temperature under N_2. The mixture was stirred for 30 min at room temperature. Evolution of a gas was detected.

Glycolaldehyde Oxime (12). A solution of glycolaldehyde (240 mg, 4.00 mmol), hydroxylamine hydrochloride (278 mg, 4.00 mmol) and triethylamine (0.56 mL, 4.0 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 12 h. The solvent was removed under reduced pressure to give an orange oil. An acetone solution of the oil was treated with *N*-(trimethylsilyl)imidazole and analyzed by GC (column A, 70 °C). Two peaks were detected with retention times of 8.4 and 10.6 min in a 2:3 ratio. The second peak had a mass spectrum (GC/MS) consistent with the bis(silylated)hydroxy oxime **12**; the identity of the first peak was not determined. The ^1H NMR of the oil showed a pair of doublets at 4.41 and 4.68 ppm consistent with the CH_2 protons of the syn and anti oxime isomers and a triplet at 6.70 ppm consistent with the HC= proton of one of the oxime isomers. The other expected triplet may have been obscured in the multiplet centered at 7.35 ppm (partially due to the unidentified compound). ^1H NMR of **12** (Me_2SO-d_6 + D_2O) δ 4.41 (d, *J* = 4 Hz, 2 H), 4.68 (d, *J* = 4 Hz, 2 H), 6.70 (t, *J* = 4 Hz, 1 H), other triplet may be in multiplet centered at 7.35 ppm; mass spectrum, *m/e* (relative intensity) 219 (M^+, 2.5), 148 (100+), 147 (100+), 130 (100+), 103 (63), 100 (65), 75 (100+), 74 (100+), 73 (100+), 66 (100+), 59 (100+).

Formaldehyde *O*-[2-(Aminooxy)ethyl]oxime (13). Aqueous formaldehyde (37%, 29 μL, 0.36 mmol) was added via syringe to a solution of **4** (32.8 mg, 0.356 mmol) in $CDCl_3$ (0.5 mL) at room temperature in a ^1H NMR tube. The monooxime **13** was formed in less than 5 min as indicated by ^1H NMR. The solution was treated with *N*-(trimethylsilyl)imidazole to silylate the monooxime; GC analysis (column A, 70 °C) gave two peaks with retention times of 2.5 (major peak) and 3.0 min (minor peak). The minor peak was the dioxime **14** and the major peak was silylated **13** as shown by GC/MS. No attempt was made to isolate the compound in a pure state: ^1H NMR of **13** ($CDCl_3$) δ 3.9 (m, 2 H), 3.75 (m, 2 H), 4.78 (br s, NH and H_2O) 6.71 (AB quartet, J_{AB} = 8 Hz, ν_{AB} = 36 Hz, 2 H); mass spectrum of silylated **13**, *m/e* (relative intensity) 177 (M^+ + H, 0.14), 146 (5.1), 119 (8.0), 103 (11), 102 (4.5), 89 (21), 75 (16), 74 (4.0), 73 (29), 59 (8.4), 58 (3.5).

Formaldehyde *O,O'*-(1,2-ethanediyl)bis(oxime) (14) was synthesized from aqueous formaldehyde and **4**:[74] mass spectrum, *m/e* (relative intensity) 117 (M^+ + H, 0.55), 116 (M^+, 0.18), 91 (9.1), 89 (4.5), 88 (100), 72 (28), 71 (29), 70 (3.0) 61 (63), 59 (4.3), 58 (84).

Formaldehyde *O*-(2-Hydroxyethyl)oxime (15). Aqueous formaldehyde (37%, 54 μL, 0.67 mmol) was added via syringe to a solution of **4** (62 mg, 0.67 mmol) in $CDCl_3$ (0.5 mL) at room temperature in a ^1H NMR tube. The monooxime **13** was formed in less than 5 min as indicated by ^1H NMR. The H_2O layer was removed and then the solvent was removed under reduced pressure to give a colorless liquid that was dissolved in CH_2Cl_2 (5 mL). Triethylamine (0.18 mL, 1.3 mmol) was added to the solution. *tert*-Butyl hypochlorite (0.15 mL, 1.3 mmol) was added via syringe to the stirred solution at –78 °C under N_2. The mixture was stirred for 10 min at –78 °C and was then allowed to come to room temperature. The solvent was removed under reduced pressure to give a residue consisting of a white solid ($Et_3N{\cdot}HCl$) and a yellow liquid. The ^1H NMR spectrum of the residue had an AB quartet centered at δ 6.75. An acetone solution of the residue was treated with *N*-(trimethylsilyl)imidazole and analyzed by GC (column A, 70 °C). The GC trace showed one major peak at 3.5 min; GC/MS showed the compound to be the silylated hydroxyoxime **15**: ^1H NMR ($CDCl_3$) δ 4.27 (m, 4 H), 6.75 (AB quartet, J_{AB} = 8 Hz, ν_{AB} = 35 Hz, 2 H); mass spectrum, *m/e* (relative intensity) 161 (M^+, 0.17), 146 (21), 117 (10), 103 (32), 102 (21), 75 (100+), 74 (8.7), 73 (100+), 61 (8.4), 59 (16), 58 (12).

1-Phenyl-1,2-ethanediol (17) was prepared in 83% yield as a white solid from **7** according to the procedure of Emerson and Agnew.[75] ^1H NMR[76a] and IR[76b] spectra of the solid matched literature spectra: mp 66–67 °C (lit.[76c] mp 67–68 °C).

Oxidation of 1-Phenyl-1,2-ethanediol (17). With nickel peroxide: a solution of **17** (247 mg, 1.79 mmol) and a suspension of nickel peroxide (2.37 g, 2.47 mol of O) in ether (15 mL) was stirred at –78 °C for 2 h. The mixture was allowed to warm to room temperature and the solid was immediately filtered off. The filtered solid was washed with ether. The ether filtrates were combined and dried ($MgSO_4$), and the ether was removed under reduced pressure to give a colorless liquid (160 mg). ^1H NMR and comparison with authentic samples showed the liquid to be a mixture of benzaldehyde and **17** in 19% and 50% yields, respectively.

The reaction was repeated except that after stirring for 2 h at –78 °C, the mixture was filtered at –78 °C and then allowed to warm to room temperature. Only **17** was isolated in 82% yield.

With *tert*-butyl hypochlorite: *tert*-butyl hypochlorite (56 μM, 0.50 mmol) was added via syringe to a stirred solution of **17** (100 mg, 0.724 mmol) and triethylamine (69 μL, 0.50 mmol) in CH_2Cl_2 (5 mL) at –78 °C. The mixture was stirred at –78 °C for 2 h and was then filtered at –78 °C. The solvent was removed under reduced pressure to give only 83.0 mg (83% yield) of **17**.

Attempted Detection of Formaldehyde in the Oxidation of 1,2-Bis(aminooxy)ethane (4). Acetylacetone reagent, used for the detection of monomeric formaldehyde, was prepared according to the procedure of Nash.[19] *tert*-Butyl hypochlorite (0.23 mL, 2.0 mmol) was added slowly via syringe to a stirred solution of **4** (92 mg, 1.0 mmol) and tributylamine (0.48 mL, 2.0 mmol) in CH_2Cl_2 (2 mL) at room temperature. Acetylacetone reagent (2 mL) was added immediately after the addition of *tert*-butyl hypochlorite. The mixture was shaken and allowed to sit at room temperature. After 1 h, no yellow-green color that would indicate the presence of monomeric formaldehyde had formed. A similar result was obtained by using nickel peroxide as oxidant.

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Determination of Nitrogen Yields in *tert*-Butyl Hypochlorite Oxidation. The 1,2-bis(hydroxylamine) and tributylamine were dissolved in toluene in the flask which was then cooled to -78 °C and flushed with argon. *tert*-Butyl hypochlorite was added via syringe to the stirred solution. The mixture was immediately allowed to warm to room temperature and was stirred for 10 min. Gas samples were taken and the percentage of nitrogen relative to argon was measured by GC (column B, 25 °C).[77] The yield of nitrogen was calculated from the percentage by using a calibration curve. Oxidation of **4** gave a 29 ± 1% yield of nitrogen (average of three injections on one sample). Oxidation of **5** gave a 21 ± 1% yield of nitrogen (average of four injections on one sample).

Determination of Nitrogen Yields in Nickel Peroxide Oxidations. To a suspension of nickel peroxide in tributylamine and toluene in a flask connected to a water-filled buret under argon was added a solution of the 1,2-bis(hydroxylamine) in toluene. The nitrogen yield was calculated from the displaced water in the buret. Qualitative analysis of the gas (GC, column B, 25 °C) showed the presence of nitrogen. Oxidation of **4** gave a 63% yield of nitrogen (single determination). Oxidation of **5** gave a 61% yield of nitrogen (single determination).

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Registry No. **1**, 6788-84-7; **2**, 91523-84-1; **3a**, 91523-85-2; **3b**, 91523-86-3; **4**, 5627-11-2; **4S** (supp), 91523-87-4; **5**, 91523-88-5; **5**·2HCl, 91523-89-6; **6**, 91523-90-9; **7**, 2425-28-7; **8**, 91523-91-0; **9**, 91523-92-1; **10**, 41252-83-9; **11**, 91523-93-2; **12**, 37110-02-4; **12S** (supp), 91523-94-3; **13**, 91523-95-4; **13S** (supp), 91523-96-5; **14**, 91523-97-6; **15**, 54722-79-1; **15S** (supp), 91523-98-7; **16**, 557-30-2; **16S** (supp), 54731-39-4; **17**, 93-56-1; **17S** (supp), 91523-99-8; **18**, 4589-97-3; **18S** (supp), 91524-00-4; **19**, 91524-01-5; **20**, 91524-02-6; **21**, 91524-03-7; **21S**, 91524-04-8; **22**, 91524-05-9; **22S**, 91524-06-0; **23**, 90005-59-7; **23S**, 91524-07-1; **24**, 25070-24-0; **24S**, 91524-08-2; **25**, 30842-07-0; **26**, 91524-09-3; **27**, 91524-10-6; **31**, 91524-11-7; **32**, 91524-12-8; 1,2-bis(phthalimidooxy)ethane, 6437-67-8; nickel peroxide, 12035-36-8; *tert*-butyl hypochlorite, 507-40-4; $C_6H_5CO_2SiMe_3$, 2078-12-8; $Me_3SiOCH_2CH_2OSiMe_3$, 7381-30-8.

Supplementary Material Available: Mass spectral data and the details of the assignments for the products from the oxidation of the 1,2-bis(hydroxylamines) (11 pages). Ordering information is given on any current masthead page.

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Reaction of Triplet Carbonyl Carbene with Olefins

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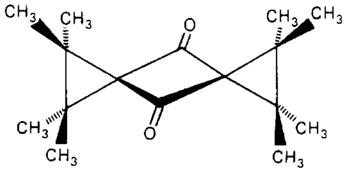
The gas-phase reaction of $C_2O(^3\Sigma)$ with 2,3-dimethyl-2-butene produces 1,1,2,2,6,6,7,7-octamethyldispiro[2.1.2.1]octane-4,8-dione and 2,2,3,3-tetramethylcyclopropanecarboxylic acid as major products rather than the allenic product characteristic of the reaction with simpler substrates. The positive identification of these molecules provides strong evidence for prior formation of the previously postulated cyclopropylideneketene. Further, the rate-determining step for reaction of $C_2O(^3\Sigma)$ with the substrate cannot be elimination of CO as has been postulated on the basis of calculations.

A series of careful experiments by Bayes et al.[1,2] has provided the basis for a recent detailed theoretical examination of the reaction of $C_2O(^3\Sigma)$ with olefins by Fukui and co-workers.[3] The Bayes group found that photolysis of C_3O_2 produced two distinct species depending upon whether or not radiation from a mercury lamp was filtered to eliminate radiation below 300 nm. The species produced with the filtered radiation was more discriminating than that made at shorter wavelengths, reacted rapidly with oxygen, and so was assigned as $C_2O(^3\Sigma)$. The less discriminating reactant was assigned as $C_2O(^1\Delta)$. Calculations[4] support the assignment of the triplet as the lower energy state, and further, Milligan and Jacox[5] have observed triplet C_2O in matrix experiments. While all available evidence supports $C_2O(^3\Sigma)$ as the species formed above 300 nm, the situation for shorter wavelength radiation is more clouded given recent work showing that $C_2O(^3\Sigma)$ is a product in multiphoton laser photolysis at 266 nm.[6] Since in this work we deal with photolysis above 300 nm, this need not concern us.

Bayes has shown that in the gas phase $C_2O(^3\Sigma)$ attacks ethylene at 150 torr to give allene as the most important end product (eq 1). In later work Willis and Bayes[2a] found

$$C_2O(^3\Sigma) + C_2H_4 \rightarrow C_3H_4 + CO \qquad (1)$$

that yields of allenes from olefins are pressure dependent, indicating existence of an intermediate which can be stabilized by loss of energy in collisions. In experiments with 2,3-dimethyl-2-butene (tetramethylethylene, TME) a solid material formed whose mass, infrared, and NMR spectra though not given were reported as consistent with those expected for 1,1,2,2,6,6,7,7-octamethyldispiro[2.1.2.1]octane-4,8-dione (ODOD), the dimer of (tetramethylcyclo-



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