Photooxygenation of 1,4-Diaza-1,3-butadienes (α-Diimines): Formation of Isonitriles

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Dye-sensitized photooxygenations of cyclic and acyclic 1,4-diaza-1,3-butadienes (α-diimines), carrying a methyl or an ethyl group in the 2-position, yield isonitriles and amides, as well as formaldehyde or acetaldehyde. Thus, cyclic α-diimines such as 5,6-dimethyl- (**1a**), 5-methyl-6-phenyl- (**1b**), 5-methyl-6-(p-tolyl)- (**1c**), and 5,6-diethyl-2,3-dihydropyrazine (**1d**) yield the respective 1-isocyano-2-(acylamino)ethanes **2a–d**, whereas 5-isopropyl-6-phenyl- (**1e**) and 5,6-diphenyl-2,3-dihydropyrazine (**1f**) are inert toward photooxygenation. Acyclic α-diimines such as 1,8-bis(acetylamino)-3,6-diaza-4,5-dimethyl-3,5-octadiene (**4a**), 2,5-diaza-3,4-dimethyl-2,4-hexadiene (**4b**), 1,4-diaza-2,3-dimethyl-1,4-diphenyl-1,3-butadiene (**4c**), and *N,N'*-bis[(1*S*,2*S*,3*S*,5*R*)-pinan-3-ylmethyl]-2,3-butanediimine (**4d**) afford the respective isonitriles **5a–d** and acetamides **6a–d**. With retention of configuration, chiral α-diimines such as (−)-*N,N'*-bis[(*S*)-1-phenylethyl]-2,3-butanediimine [(*S,S*)-**4e**] and its *R,R* enantiomer [(*R,R*,)-**4e**], and (3*S*,8*S*)-(−)-3,8-dicarbomethoxy-4,7-diaza-2,5,6,9-tetramethyl-4,6-decadiene [(*S,S*)-**4f**] yield the corresponding enantiomerically pure isonitriles (*S*)-**5e**, (*R*)-**5e**, and (*S*)-**5f** and acetamides (*S*)-**6e**, (*R*)-**6e**, and (*S*)-**6f**. Evidence for a singlet oxygen reaction is presented. A working hypothesis is proposed which includes the formation of a transient hydroperoxide **7** that fragments into an isonitrile molecule, an aldehyde, and an *N*-alkyl- or *N*-arylnitrilium cation and a hydroxide ion; the latter combine to yield the amide groups in **2a–d** and the amide compounds **6a–f**.

Introduction

Numerous examples for Diels–Alder reactions with singlet oxygen ($^1O_2$) as the dienophile have been published. In most cases, the reactive *cis*-1,3-butadiene grouping is incorporated in nonaromatic or in carbo- and heteroaromatic ring systems such as cyclopentadienes, anthracenes, and furans, respectively.[1] Acyclic 1,3-butadienes have been studied to a much lesser extent. Depending upon substitution, acyclic 1,3-butadienes may undergo ene reactions and [2 + 2] cycloadditions along with the Diels–Alder reaction.[2]

Replacement of one carbon atom in the 1,3-butadiene moiety by a nitrogen atom leads to 1-aza- and 2-aza-1,3-butadienes. Of these, the 2-aza-1,3-butadiene group contained in heteroaromatics such as oxazoles[3,4] and imidazoles[5,6] reacts readily with $^1O_2$. However, the 1-aza-1,3-butadiene group, as contained in isoxazoles, was shown to be inert toward singlet oxygen.[4]

By replacing two carbon atoms of the 1,3-butadiene group by nitrogen atoms, 1,2-diaza-, 1,3-diaza-, 1,4-diaza-, and 2,3-diaza-1,3-butadienes are obtained. But apparently, only 2,3-diaza-1,3-butadienes such as azines and 1,3,4-oxadiazoles and 1,4-diaza-1,3-butadienes such as 1,2,5-oxadiazoles (furazanes) have been studied. Whereas azines are reported to react with $^1O_2$ via various pathways,[7] 1,3,4- and 1,2,5-oxadiazoles turned out to be inert toward singlet oxygen.[4]

To the best of our knowledge, 5,6-diphenyl-2,3-dihydropyrazine (**1f**) is the only other 1,4-diaza-1,3-butadiene (α-diimine) that has been studied. However, this compound was photoisomerized to 1-methyl-4,5-diphenylimidazole before it reacted with singlet oxygen to 1,3-dibenzoylurea in a multistep reaction.[8]

In a previous short communication, we showed that *unrearranged* **1f** is inert toward $^1O_2$.[9] By replacing one or both phenyl groups of **1f** by a methyl group, the resulting 5-methyl-6-phenyl- (**1b**) and 5,6-dimethyl-2,3-dihydropyrazine (**1a**) became susceptible to oxygenation in the presence of typical singlet oxygen producing sensitizers in various solvents. To our surprise, isonitriles **2b** and **2a**, respectively, were formed in appreciable amounts.[9]

This result appeared to be interesting enough to be followed up. Firstly, we extended our studies to 5,6-diethyl- (**1d**) and 5-isopropyl-6-phenyl-2,3-dihydropyrazine (**1e**), in order to see whether alkyl groups other than methyl are suitable substituents that are oxidized and eliminated during the oxygenation process.

Secondly, to determine whether *acyclic* N-alkyl- and N-aryl-substituted 1,4-diaza-1,3-butadienes, carrying at least one methyl group in the 2-position, are also transformed into isonitriles, we studied the following symmetrically N,N'-disubstituted 2,3-butanediimines: 1,8-bis(acetylamino)-3,6-diaza-4,5-dimethyl-3,5-octadiene (**4a**), 2,5-diaza-3,4-dimethyl-2,4-hexadiene (**4b**), 1,4-diaza-2,3-dimethyl-1,4-diphenyl-1,3-butadiene (**4c**), and *N,N'*-bis[1*S*,2*S*,3*S*,5*R*)-pinan-3-ylmethyl]-2,3-butanediimine (**4d**).

Finally, after we had obtained positive results with α-diimines **4a–d**, we became interested to study optically active α-diimines, the chiral centers of which are directly attached to the imino nitrogen atom. We chose to use (−)-*N,N'*-bis[(*S*)-1-phenylethyl]-2,3-butanediimine [(*S,S*)-**4e**] and its *R,R* enantiomer [(*R,R*)-**4e**] and (3*S*,8*S*)-(−)-3,8-dicarbomethoxy-4,7-diaza-2,5,6,9-tetramethyl-4,6-decadiene [(*S,S*)-**4f**] as substrates.

(1) Reviews: (a) Gollnick, K.; Schenck, G. O. In *1,4-Cycloaddition Reactions; the Diels–Alder Reaction in Heterocyclic Syntheses*; Hamer, J., Ed.; Academic Press: New York, 1967; p 255. (b) Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1. (c) Rigaudy, J. *Pure Appl. Chem.* **1968**, *16*, 169. (d) Wasserman, H. H.; Lipshutz, B. H. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Vol. 40, Organic Chemistry, p 429. (e) Saito, I.; Matsuura, T. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., *Eds.*; Academic Press: New York, 1979; Vol. 40, Organic Chemistry, p 511. (f) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (g) Wasserman, H. H.; Ives, J. L. *Tetrahedron* **1981**, *37*, 1825. (h) Frimer, A. A. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. II.

(2) (a) Hasty, N. M.; Kearns, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3380. (b) Manring, L. E.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4710. (c) Gollnick, K.; Griesbeck, A. *Tetrahedron* **1984**, *40*, 3235.

(3) Review: Wasserman, H. H.; McCarthy, K. E.; Prowse, K. S. *Chem. Rev.* **1986**, *86*, 845.

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(5) Reviews: (a) Matsuura, T.; Saito, I. In *Photochemistry of Heterocyclic Compounds*; Buchardt, O., Ed.; J. Wiley: New York, 1976; p 456. (b) George, M. V.; Bhat, V. *Chem. Rev.* **1979**, *79*, 447.

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(7) (a) Lechtken, P. Z. *Naturforsch. B* **1976**, *31*, 1436. (b) Landis, M. E.; Maudoux, D. C. *J. Am. Chem. Soc.* **1979**, *101*, 5106. (c) Ando, W.; Sato, R.; Sonobe, H.; Akasaka, T. *Tetrahedron Lett.* **1984**, *25*, 853.

(8) Bhat, V.; George, M. V. *J. Org. Chem.* **1979**, *44*, 3288.

(9) Gollnick, K.; Koegler, S. *Tetrahedron Lett.* **1988**, *29*, 1127.

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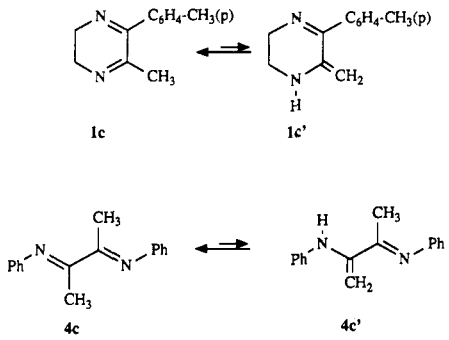
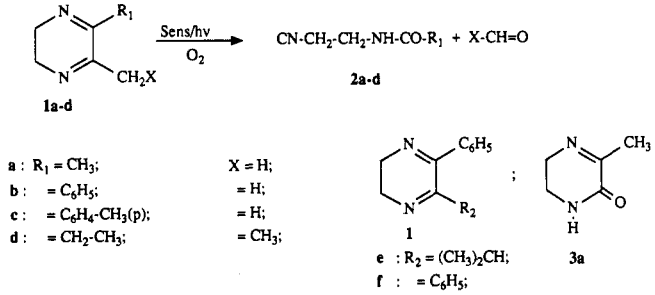
Scheme I. Possible α-Diimine ⇄ α-Imino Enamine Equilibrium



Scheme II. Dye-Photosensitized Oxygenation of 2,3-Dihydropyrazines



Results

Irradiation under Nitrogen. To check the photochemical stabilities of α-diimines, compounds **1a**, **1b**, **1f**, and **4a** were irradiated for several hours in deoxygenated solvents in the absence (λ_{exc} > 380 nm, MeCN) and in the presence of photosensitizers such as rose bengal (RB) in MeCN or acetone (λ_{exc} > 490 nm) and tetraphenylporphin (TPP) in $CHCl_3$, CH_2Cl_2, or CCl_4 (λ_{exc} > 490 nm). As their ^1H NMR spectra showed, the acyclic as well as the cyclic α-diimines remained unaltered. In each case, the starting α-diimine was quantitatively recovered.

Irradiation under Nitrogen in the Presence of CD_3OD. According to the ^1H NMR spectra of the α-diimines 1 and 4, there is no indication for the presence of an equilibrium α-diimine ⇄ α-imino enamine such as **1c** ⇄ **1c′** or **4c** ⇄ **4c′**. However, the NMR results only show that the ratio of [α-diimine] to [α-imino enamine] should be better than about 20:1 (Scheme I).

In spite of such an unfavorable equilibrium, the presence of α-imino enamines could be responsible for product formation, since enamines are very efficient substrates for $^1O_2$ reactions.[10] Therefore, in order to check whether such an equilibrium exists at all, we treated the 2,3-dihydropyrazine derivative **1c** and the acyclic α-diimine **4c** for several hours in deoxygenated MeCN/CD_3OD (1:1, v/v) in the dark as well as in the presence of RB and light. If **1c′** and **4c′** were present, they should undergo a rapid H/D exchange, thus leading to a successive replacement of the methyl protons of the CH_3 group at C-5 of **1c** and of the methyl protons of **4c** by deuterium. The methyl group of the *p*-tolyl substituent of **1c** and the aromatic hydrogens of the phenyl groups of **4c** would, of course, remain unchanged and could therefore serve as internal standards. Under both the thermal and photochemical reaction conditions, the 1:1 ratio of the integrals of the ^1H NMR singlets at δ 2.06 and 2.33 of **1c** and the 6:10 ratio of the signals at δ 2.13 and 6.75–7.39 of **4c** remained unaltered, indicating that tautomers **1c′** and **4c′** do not play any role in reactions of α-diimines.

Photooxygenation of 2,3-Dihydropyrazines. When 2,3-dihydropyrazines **1a–d** were irradiated in oxygen-saturated solvents in the presence of RB or TPP (λ_{exc} = 480 to 570 nm) at 13 °C, each of these substrates consumed 1 molar equiv of O_2. Under the same conditions, 2,3-dihydropyrazines **1e** and **1f** remained unchanged and were recovered quantitatively.

At low temperatures (−50 to <−20 °C), no oxygen was absorbed for several hours by **1a** (2×10^{-1} M) in $CDCl_3/CFCl_3$ (1:3) when irradiated in the presence of TPP as a sensitizer. At −20 °C, this solution absorbed 1 molar equiv of O_2 within 14 h, whereas at 13 °C the same consumption occurred within about 4 h.[11] The product composition was the same at both temperatures.

The products isolated from oxygenations of **1a–d** were formaldehyde (from **1a–c**) or acetaldehyde (from **1d**), identified qualitatively by the appropriate spot tests,[12] and isonitriles **2a–d**, obtained as colorless crystals in yields of about 50% after sublimation (Scheme II).

All the ^1H NMR spectra of the 1-isocyano-2-(acylamino)ethanes **2a–d** contain a multiplet in the region of δ 3.4–3.6 for the $-CH_2CH_2-$ group and a broad signal at about δ 6.3–6.9 for the NH group. In the ^{13}C NMR spectra, the triplet at δ 157 is a distinctive of the isonitrile-^{13}C resonance; a triplet of a triplet, observed at about δ 41, is expected to occur for the carbon atom of the methylene group located next to the isonitrile group. In agreement with values reported for isonitrile-N signals of ^{14}N NMR spectra,[13] these signals appear at δ−209. The IR spectra of **2a–d** all contain the typical strong absorption band of the isocyano group at about 2150 cm^{-1}.

However, the ^1H NMR spectra of the original product solutions indicate the presence of an additional compound in each case, showing, for example, signals at δ 2.18 (s), 3.62 (m), and 4.86 (m) in a ratio of 3:4:2 when **1a** is employed as the O_2 acceptor.[9] 3-Methyl-5,6-dihydro-2(1*H*)-pyrazinone (**3a**),[14] which we suspected to be a potential oxygenation product, is not present in the product mixture (^1H NMR spectrum).

We have not yet isolated the byproducts. However, we found, e.g., a constant ratio of the CH_3 singlets at δ 1.98 (**2a**) and 2.18 (byproduct) of about 1:1 during the photooxygenation of **1a** at 13 °C (about 4 h, see above). When the final 1:1 product mixture was heated to 50 °C in the presence of benzene as an inert standard and kept at this temperature for several hours, the CH_3 singlets of **2a** increased at the expense of those of the byproduct, until after 25 h a 4:1 ratio of these signals was obtained. After another 10 h at 50 °C, some new ^1H NMR signals began to appear. The results show that the unknown byproduct cannot be the precursor of isonitrile **2a** that is formed during the photooxygenation of **1a** at 13 °C.

Photooxygenation of Acyclic α-Diimines. Each of the symmetrically N,N′-disubstituted 2,3-butanediimines **4a–f** absorbed 1 molar equiv of oxygen when irradiated in O_2-saturated MeCN in the presence of RB (λ_{exc} =

(10) Review: Schaap, A. P.; Zaklika, K. A. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Vol. 40, Organic Chemistry, p 173.

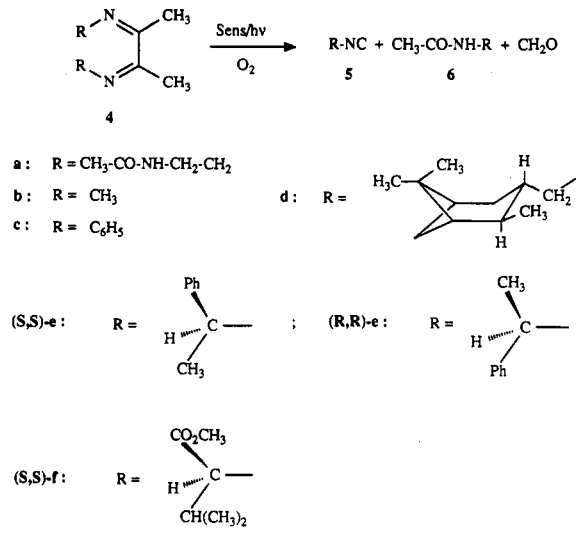
(11) The oxygenation rate increases with increasing solvent polarity. Thus, in nonpolar CCl_4 at 13 °C, less than 50% of **1a** had reacted in 4 h under otherwise identical conditions. Kinetic studies are under way.

(12) Feigl, F. *Tüpfelanalyse*; Akademische Verlagsgesellschaft: Frankfurt, 1960; Vol. 2.

(13) Stephany, R. W.; deBie, M. J. A.; Drenth, W. *Org. Magn. Res.* **1974**, *6*, 45.

(14) Masuda, H.; Yoshida, M.; Shibamoto, T. *J. Agric. Food Chem.* **1981**, *29*, 944.

Scheme III. Dye-Photosensitized Oxygenation of 2,3-Butanediimines



480–570 nm). Isonitriles **5a–f** (**5a** = **2a**) and acetamides **6a–f** were isolated at appreciable yields in ratios of about 1:1, and the formation of formaldehyde was qualitatively proved by the appropriate spot test. In contrast to the results obtained with 2,3-dihydropyrazines, the formation of byproducts was not observed (Scheme III).

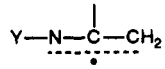
When the N,N′-disubstituted 2,3-butanediimines carried chiral substituents as in **4d–f**, the substituents in the resulting isonitriles **5d–f** and acetamides **6d–f** retained their configurations. This outcome may not be surprising for products **5d** and **6d**, where the asymmetric C atoms are separated from the N atoms by at least one CH_2 group. But it is worth mentioning for isonitriles (*S*)-**5e**, (*R*)-**5e**, and (*S*)-**5f** and acetamides (*S*)-**6e**, (*R*)-**6e**, and (*S*)-**6e**, where the stereogenic C atoms are attached to the corresponding N atoms. These latter results may make the isonitrile synthesis from α-diimines a useful addition to the already existing isonitrile syntheses because photosensitized oxygenations are carried out under rather mild conditions (neutral aprotic polar and nonpolar solvents, low temperatures, etc.).

Discussion

The products, isolated from dye-photosensitized oxygenations of α-diimines, are undoubtedly secondary products. At least one precursor is required to afford these products, the most likely candidate being an unstable hydroperoxide **7** that fragments into an isonitrile (or isonitrile group), an aldehyde, a hydroxide anion, and a stabilized nitrilium cation; the latter immediately combine to give an amide (or amide group) (Scheme IV).

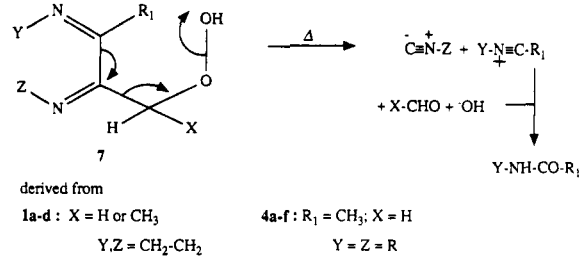
However, hydroperoxide **7** is not a primary product either. It should be produced in a reaction sequence according to one of the following three basic mechanisms.

Type I, 1.[15] This type of photooxygenation is induced by a hydrogen-atom transfer from the substrate to the electronically excited sensitizer. With α-diimines **1** and **4**, allylic radicals such as



1•, 4•

Scheme IV. Proposed Fragmentation of Hydroperoxides 7 into Isonitriles, Amides, and Aldehydes



could be formed that add $^3O_2$ and a hydrogen atom (in a chain or nonchain reaction) to yield **7**. But this reaction sequence is rather unlikely to occur because, firstly, photooxygenation of **1a** is not quenched by radical scavengers such as phenols and triphenylmethane and, secondly, no sensitizer bleaching was observed and α-diimines **1** and **4** remained unchanged when irradiations were carried out in degassed solvents, indicating that electronically excited RB and TPP are incapable to dehydrogenate substrates **1** and **4**.

Type I, 2. Photooxygenations of this type are induced by an electron transfer from the substrate to the electronically excited sensitizer (sens*) yielding sens$^{\bullet-}$ and the radical cation of the substrate. With α-diimines **1** and **4** as substrates, subsequent reactions of $\mathbf{1}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ with $^3O_2$ or $O_2^{\bullet-}$ could afford finally **7**. However, with singlet and triplet excited rose bengal, ^{1}RB* and ^{3}RB*, electron abstraction is efficient only with substrates having oxidation potentials less than about 1.1 and 0.7 V, respectively,[17] whereas **1a**, for example, has an oxidation potential (E_{ox}) of 1.51 V in MeCN. Furthermore, photooxygenation of **1** and **4** occurs efficiently in nonpolar solvents, a result that renders the electron-transfer-induced photooxygenation pathway also highly unlikely.

Type II. This type of photooxygenation requires an energy transfer from sens* to $^3O_2$ producing singlet molecular oxygen ($^1O_2$, $^1\Delta_g$) as the reactive intermediate. Triplet excited dyes such as ^{3}RB* and ^{3}TPP* are well-known generators of $^1O_2$. Therefore, whenever substrates are oxidized in the presence of light and RB or TPP in polar and nonpolar solvents, singlet oxygen is supposed to be responsible for the oxygenation reaction. The rate-decreasing effect of DABCO on the photooxygenation of the α-diimines supports this supposition.

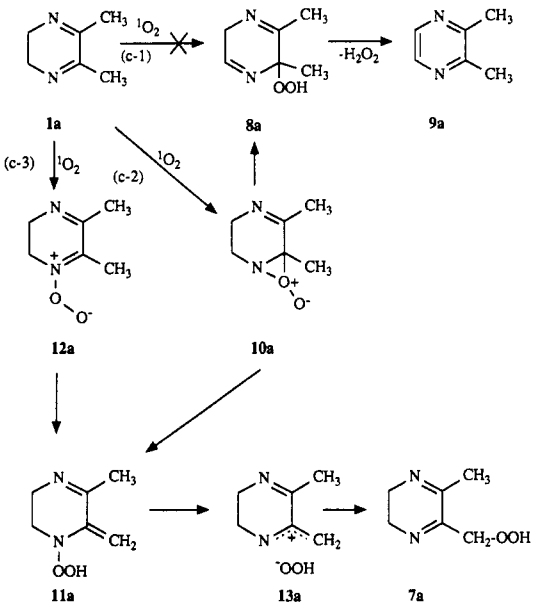
For $^1O_2$ reactions with α-diimines, several pathways may be considered: (a) Electron-transfer between $^1O_2$ and an α-diimine in MeCN could produce superoxide, $O_2^{\bullet-}$, and an α-diimine radical cation ($\mathbf{1}^{\bullet+}$, $\mathbf{4}^{\bullet+}$) that may finally afford **7**. However, such a process may occur with appreciable rates only if E_{ox} of the substrate is less than 0.7 V and if the substrate radical cation reacts with $^3O_2$ in a chain reaction having a rather long chain length.[17] The oxidation potentials of α-diimines exclude this mechanism.

(b) An attractive mechanism for the formation of hydroperoxide **7** would be an ene-type reaction of $^1O_2$ with the enamine moiety of the tautomeric α-imino enamine (**1c′**, **4c′**). However, this type of reaction is excluded because neither the ^{1}H NMR spectra of **1c** and **4c** nor the H/D exchange experiments give any hint that tautomers **1c′** and **4c′** are present even in minute amounts.

(c) Therefore, the most likely reaction of $^1O_2$ with the α-diimine is the addition of singlet oxygen to either the C or N atom or to the C–N double bond of the –N=

(15) For definitions, see refs 1b and 16.
(16) Gollnick, K. *Chim. Ind.* (*Milan*) **1982**, *64*, 156.
(17) Gollnick, K.; Held, S. *J. Photochem. Photobiol., A: Chem.* **1991**, *59*, 55.

Scheme V. Possible Pathways for Singlet Oxygen Reactions with α-Diimines Such as 1a



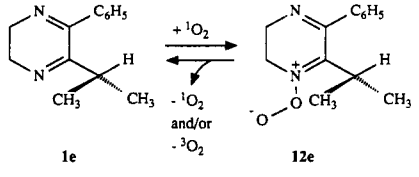
CCH_2X (X = H or CH_3) moiety (Scheme V).

Path c-1. If $^1O_2$ interacts with C-5 of **1a**, it may either yield a zwitterion or it may react in an ene-type reaction with the ring-CH_2 group that is attached to N. Both modes of reaction are unlikely to occur, since neither hydroperoxide **8a**[18] nor its possible H_2O_2-elimination product, pyrazine **9a**, was obtained.

Path c-2. If $^1O_2$ adds to the C–N double bond of **1a**, the ensuing *endo*- and *exo*-peroxaziridines (**10a**) should give rise to **8a** and hydroperoxide **11a**, respectively. Since **8a** (or **9a**) is not observed, path c-2 is considered less likely than the following path c-3.

Path c-3. If $^1O_2$ attaches to the N-atom of **1a**, a zwitterion **12a** (a "pernitrone" or "nitrone oxide" of **1a**) results that may be transformed via hydroperoxide **11a** and ion pair **13a** into hydroperoxide **7a**.

Mechanism c-3 explains easily the photooxygenation of the cyclic and acyclic α-diimines, **1b–d** and **4a–f**, as well as the inertness of **1e** and **1f** toward singlet oxygen. The inertness of the isopropyl-substituted 2,3-dihydropyrazine **1e** toward $^1O_2$ requires an explanation. Inspection of space-filling models indicates that free rotation of the isopropyl group about the C-C bond between C-5 and the $CH(CH_3)_2$ group should be restricted. The conformation, in which the tertiary isopropyl-H atom is located in-plane with the dihydropyrazine ring pointing toward the phenyl group at C-6, appears to be the most stable one for **1e** as well as for **12e**. However, conformation **12e** is inappropriate for the required proton-transfer.[19]



(18) A corresponding interaction of $^1O_2$ with the nitrone derived from 2,4,4-trimethyl-1-pyrroline, yielding the nitrone of 5-hydroperoxy-3,3,5-trimethyl-1-pyrroline, has been observed: Ching, T.-Y.; Foote, C. S. *Tetrahedron Lett.* **1976**, 3771.

(19) Similar results are observed with 1,1-dimethyl-2-isopropylethylene[1b,20] and 1,1,3,3-tetraarylpropenes,[21] where the teritary allylic hydrogens are sterically unavailable for the ene-reaction with singlet oxygen.

Conclusion

Dye-photosensitized oxygenations of suitably alkyl-substituted α-diimines (1,4-diaza-2-methyl(or ethyl)-1,3-butadienes) occur as singlet oxygen reactions. The 2-alkyl group, essential for the oxygenation reaction to proceed, is transformed into a carbonyl compound, whereas the rest of the α-diimine molecules undergoes a fragmentation into a 1:1 mixture of an isonitrile and an amide (or into a 1-isocyano-2-(acylamino)ethane from 2,3-dihydropyrazines). The most likely precursor of these products is an unstable hydroperoxide **7**. Arguments for its formation via reaction sequence c–3 of Scheme V are presented. Though no direct proof of intermediate **7** is yet available, the assumption of its formation and ensuing fragmentation (Scheme IV) represents a useful working hypothesis for further investigations.[22]

Experimental Section

Solvents and commercially available compounds were purchased from standard suppliers and purified to match reported physical constants and spectral data. Melting points are uncorrected.

^1H and ^{13}C NMR spectra were recorded with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. ^{14}N NMR spectra were recorded with $CDCl_3$ as solvent and sodium nitrate as internal standard. IR spectra were taken in KBr. Mass spectra were taken at 70 eV. Oxidation potentials (E_{ox}) were measured by cyclic voltammetry on a cyclic voltammograph CV-1B (Bioanalytical Systems, Inc.) at a platinum electrode vs the standard calomel electrode (SCE) in Ar-saturated MeCN. The supporting electrolyte was tetraethylammonium tetrafluoroborate (0.1 M); scan speed 400 mV/s. All the α-diimines showed irreversible oxidation potentials. The instrument was calibrated by using 1,3,5-trimethoxybenzene (E_{ox} = 1.49 V) as a standard.[24]

Preparation of Starting Material. General Procedure. 2,3-Dihydropyrazines **1a–f** were synthesized by condensation of 1,2-diaminoethane with the appropriate α-diketones. Similarly, acyclic α-diimines **4a–f** were prepared from diacetyl and 2 mol equiv of the appropriate primary amines.

5,6-Dimethyl-2,3-dihydropyrazine (1a). Yellowish oil, bp 67 °C (13 Torr) [lit.[25] bp 52–54 °C (12 Torr)]. ^1H NMR: δ 2.10 (s, 6 H), 3.26 (s, 4 H). E_{ox}: 1.51 V.

5-Methyl-6-phenyl-2,3-dihydropyrazine (1b). According to the procedure of ref 25, 1,2-diaminoethane (2 g, 34 mmol) and 1-phenyl-1,2-propanedione (5 g, 34 mmol) gave 4.6 g of **1b** (yellowish crystals, from ether/*n*-hexane; yield 80%), mp 38–39 °C. ^1H NMR; δ 2.08 (s, 3 H), 3.50 (s, 4 H), 7.35 (s, 5 Ar H). IR: 2948, 2843, 1636, 1585, 1572, 1446, 1437, 1375, 1246, 1221 cm^{-1}. MS: m/e = 172. E_{ox}: 1.52 V. Anal. Calcd for $C_{11}H_{12}N_2$ (172.23): C, 76.71; H, 7.02; N, 16.30. Found: C, 76.70; H, 7.00; N, 16.20.

5-Methyl-6-(4-methylphenyl)-2,3-dihydropyrazine (1c). 1,2-Diaminoethane (1.1 g, 19 mmol) and 1-(4-methylphenyl)-1,2-propanedione[26] (3.1 g, 19 mmol) afforded 2.5 g of **1c** (yellowish needles, from ether/ethanol; yield 75%), mp 36–37 °C: ^1H NMR: δ 2.06 (s, 3 H), 2.33 (s, 3 H), 3.41 (s, br, 4 H), 7.06–7.43 (m, 4 Ar H). E_{ox}: 1.57 V. Anal. Calcd for $C_{12}H_{14}N_2$ (186.25): C, 77.38; H, 7.58; N, 15.04. Found: C, 77.74; H, 7.61; N, 14.88.

5,6-Diethyl-2,3-dihydropyrazine (1d). 1,2-Diaminoethane (2.0 g, 34 mmol) and 3,4-hexanedione (3.88 g, 34 mmol) gave 2.8

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(22) Studies directed toward the preparation of hydroperoxides **7** by other methods are presently being carried out. Studies of suitably substituted monoimines, $RN{=}C(X)CH_3$, yielding RNC + CH_2O + XOH (e.g., with X = –COR′ affording $R'CO_2H$ as XOH), have been carried out. The results will be published elsewhere.[23]

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g of **1e** (yellowish oil; yield 55%), bp 88–89 °C (13 Torr) [lit.[25] bp 61–65 °C (11 Torr.)]. ^{1}H NMR: δ 1.13 (t, 6 H), 2.43 (q, 4 H), 3.34 (s, 4 H).

5-Isopropyl-6-phenyl-2,3-dihydropyrazine (1e). 1,2-Diaminoethane (1.5 g, 26 mmol) and 3-methyl-1-phenyl-1,2-butanedione (3.3 g, 26 mmol) led to 2.9 g of **1e** (yellowish crystals; yield 58%), mp 43–44 °C. ^{1}H NMR: δ 1.03 (d, 6 H), 2.84 (m, 1 H), 3.45 (s, 4 H), 7.38 (s, 5 Ar H). Anal. Calcd for $C_{13}H_{16}N_2$ (200.28): C, 77.96; H, 8.05; N, 13.99. Found: C, 78.47; H, 8.01; N, 13.49.

5,6-Diphenyl-2,3-dihydropyrazine (1f). Yellowish crystals, mp 162–164 °C (lit.[27] mp 161.5–162.5 °C). ^{1}H NMR: δ 3.62 (s, 4 H), 7.20 (m, 10 Ar H). E_{ox}: 1.45 V.

1,8-Bis(acetylamino)-3,6-diaza-4,5-dimethyl-3,5-octadiene (4a). According to the procedure of ref 28, 1-acetylamino-2-aminoethane[29] (6.12 g, 60 mmol) and diacetyl (2.5 g, 30 mmol) gave 3.2 g of **4a** (colorless crystals, from ether/ethanol; yield 42%), mp 164–165 °C. ^{1}H NMR: δ 1.96 (s, 6 H, N=CCH$_3$), 2.03 (s, 6 H, –COCH$_3$), 3.48 (m, 8 H, –CH$_2$CH$_2$–), 5.90 (s, 2 H, –NH–). Anal. Calcd for $C_{12}H_{22}N_4O_2$ (254.34): C, 56.67; H, 8.72; N, 22.03. Found: C, 56.73; H, 8.76; N, 22.18.

2,5-Diaza-3,4-dimethyl-2,4-hexadiene (4b). According to the procedure of ref 30, methylamine (1.86 g, 60 mmol) and diacetyl (2.6 g, 30 mmol) afforded 1.0 g of **4b** (yellowish oil; yield 30%), bp 23–25 °C (13 Torr). ^{1}H NMR: δ 2.00 (s, 6 H, CCH$_3$), 3.28 (s, 6 H, NCH$_3$). Anal. Calcd for $C_6H_{12}N_2$ (112.18): C, 64.24; H, 10.78; N, 24.98. Found: C, 63.86; H, 10.72; N, 24.70.

1,4-Diaza-2,3-dimethyl-1,4-diphenyl-1,3-butadiene (4c). Yellowish crystals, mp 138–139 °C (lit.[30] mp 139–140 °C). ^{1}H NMR: δ 2.13 (s, 6 H), 6.65–7.39 (m, 10 Ar H). E_{ox}: 1.40 V.

***N,N'*-Bis[(1*S*,2*S*,3*S*,5*R*)-pinan-3-ylmethyl]-2,3-butanediimine (4d).** Yellow crystals (yield 51%), mp 38–40 °C (lit.[31] mp 38–40 °C). ^{1}H NMR: δ 1.02 (s, 6 H), 1.13 (s, 6 H), 1.20 (s, 6 H), 2.0 (m, 16 H), 2.05 (s, 6 H), 3.38 (m, 4 H). E_{ox}: 1.39 V.

(2*S*,7*S*)-(–)-3,6-Diaza-4,5-dimethyl-2,7-diphenyl-3,5-octadiene ((–)-*N,N'*-Bis[(*S*)-1-phenylethyl]-2,3-butanediimine) [(*S,S*)-4e]. Yellow oil (yield 61%) (lit.[31] yield 66%). ^{1}H NMR: δ 1.43 (s, 6 H), 2.13 (s, 6 H), 4.70 (q, 2 H), 7.25 (m, 10 Ar H). $[\alpha]_D^{20}$: –69.2° (ethanol, *c* = 10.4). E_{ox}: 1.44 V.

(2*R*,7*R*)-(+)-3,6-Diaza-4,5-dimethyl-2,7-diphenyl-3,5-octadiene ((+)-*N,N'*-Bis[(*R*)-1-phenylethyl]-2,3-butanediimine) [(*R,R*)-4e]. (*R,R*)-4e was prepared according to the procedure described for (*S,S*)-4e.[31] Yellow oil (yield 60%). $[\alpha]_D^{20}$: +68.1° (ethanol, *c* = 10.2). ^{1}H NMR: δ 1.49 (s, 6 H), 2.19 (s, 6 H), 4.70 (q, 2 H), 7.25 (m, 10 Ar H). E_{ox}: 1.44 V.

(3*S*,8*S*)-(–)-3,8-Dicarbomethoxy-4,7-diaza-2,5,6,9-tetramethyl-4,6-decadiene [(*S,S*)-4f]. L-(+)-Valine methyl ester (7.0 g, 54 mmol) and diacetyl (4.6 g, 54 mmol) gave 3.9 g of (*S,S*)-**4f** (yellowish oil; yield 58%), bp 105–107 °C (10^{-3} Torr). ^{1}H NMR: δ 0.93 (d, 12 H), 1.75–2.50 (m, 2 H), 2.10 (s, 6 H), 3.68 (s, 6 H), 4.0 (d, 2 H). $[\alpha]_d^{20}$: –210.8° (ethanol, *c* = 5.7). E_{ox}: 1.41 V. Anal. Calcd for $C_{16}H_{28}N_2O_4$ (312.40): C, 61.51; H, 9.03; N, 8.97. Found: C, 61.42; H, 8.91; N, 8.94.

General Procedures for Photooxygenations and Irradiations under Nitrogen. A 25-mL irradiation unit with automatic O_2 consumption recording system[32] was used for photooxygenation studies. The irradiation unit, the oxygen burette, and the tubings connecting the unit with the burette were kept at 13 ± 0.1 °C by cooling with water, using a Julabo-P thermostat. A 150-W halogen lamp (Philips) and a band filter transparent between 500 and 595 nm (Hoya) as well as a mercury high-pressure lamp (Philips, HP 125 W) and a glass filter GG 14 (Schott, Mainz, cut-off at 490 nm) were employed for electronic excitation of rose bengal (RB) (3×10^{-4} M) in acetonitrile (MeCN) and of tetraphenylporphin (TPP) (5×10^{-4} M) in CCl_4. Starting concentrations of α-diimines were always 4×10^{-2} M. The solutions were saturated with oxygen before irradiation.

For low-temperature photooxygenations (about 0 to –50 °C), a 25-mL flask used as the irradiation vessel was surrounded by a cooling jacket through which an evacuated tube ("irradiation window") was fixed to the reaction vessel. Cooling, provided by using an ultrakryostat (Lauda, UK 60 SDW), leads to a thick layer of ice around the whole irradiation vessel with the exception of the "irradiation window".

The same irradiation cells, light sources, and light filters were employed for irradiations of deoxygenated solutions in the presence of sensitizers. When the α-diimine solutions were irradiated in the absence of a sensitizer, a glass filter GWV (Glashütte Wertheim, cut-off at 373 nm) was employed. During the irradiations of deoxygenated solutions, the cell was disconnected from the oxygen burette and the recording system, and the solutions were saturated with oxygen-free nitrogen by passing N_2 through the solutions for 15 min before irradiations were commenced.

Preparative Photooxygenation of α-Diimines. For preparative purposes, irradiations of 25 mL of oxygen-saturated MeCN solutions containing RB (3×10^{-4} M) and the respective α-diimine (about 4 to 8×10^{-2} M) were carried out. After the oxygen uptake ceased, MeCN was removed at a rotor evaporator at room temperature. The residues were treated as described below.

1-Isocyano-2-(acetylamino)ethane (2a). 5,6-Dimethyl-2,3-dihydropyrazine (**1a**) (200 mg, 1.8 mmol) absorbed 1 molar equiv of O_2 within 4 h. After removal of MeCN, distillation of the residue at 90 °C (10^{-4} Torr) gave yellowish crystals; sublimation at 100 °C (10^{-4} Torr) yielded 125 mg (55%) of colorless crystals **2a**, mp 73–75 °C. ^{1}H NMR: δ 1.98 (s, 3 H), 3.47 (m, 4 H), 6.32 (m, 1 H). ^{13}C NMR: δ 23.0 (q), 38.8 (t), 41.7 (tt, J_{CN} = 6.7 Hz), 157.3 (t, J_{CN} = 5.2 Hz), 170.9 (s). ^{14}N NMR: δ –209.0. IR: 3260, 3077, 2158, 2150 (–N=C), 1657, 1653 (amide I), 1558 cm^{-1} (amide II). MS: *m/e* 112 (M$^+$, 1), 85 (8), 69 (4), 43 (96), 30 (100). Anal. Calcd for $C_5H_8N_2O$ (112.06): C, 53.54; H, 7.19; N, 24.99. Found: C, 53.38; H, 7.33; N, 24.77.

3-Methyl-5,6-dihydro-2(1*H*)-pyrazinone (3a) was prepared after ref 14 for comparison: mp 98–100 °C. ^{1}H NMR: δ 2.18 (s, 3 H), 3.37 (m, 2 H), 3.67 (m, 2 H), 7.35 (s, br, 1 H). ^{13}C NMR: δ 21.0 (q), 38.9 (t), 47.4 (t), 158.5 (s), 163.5 (s). IR: 1635, 1637 (amide I), 1685 cm^{-1} (six-ring lactam).

1-Isocyano-2-(benzoylamino)ethane (2b). 5-Methyl-6-phenyl-2,3-dihydropyrazine (**1b**) (187 mg, 1.09 mmol) absorbed 1 molar equiv of O_2 within 6 h. After removal of MeCN, the residue was dissolved in CH_2Cl_2/ether (3:2, v/v). After filtration from the undissolved dye, removal of the solvents at 20 °C (12 Torr), and treatment of the yellow oil with *n*-pentane, a yellow solid was obtained; sublimation at 120 °C (10^{-4} Torr) yielded 90 mg (46%) of colorless crystals **2b**, mp 79–81 °C. ^{1}H NMR: δ 3.61 (dd, 4 H), 6.95 (m, 1 H), 7.17–7.90 (m, 5 Ar H). ^{13}C NMR: δ 39.2 (t), 41.7 (tt, J_{CN} = 6.7 Hz), 157.4 (t, J_{CN} = 4.9 Hz), 168.0 (s). ^{14}N NMR: δ –209.4. IR: 3261, 3084, 2153 (–N=C), 1651, 1642 (amide I), 1558 cm^{-1} (amide II). MS: *m/e* 174 (M$^+$, 2), 146 (3), 105 (100), 77 (15). Anal. Calcd for $C_{10}H_{10}N_2O$ (174.09): C, 68.94; H, 5.79; N, 16.08. Found: C, 68.66; H, 5.75; N, 16.22.

1-Isocyano-2-(*p*-toluylamino)ethane (2c). 5-Methyl-6-(*p*-tolyl)-2,3-dihydropyrazine (**1c**) (372 mg, 2 mmol) absorbed 1 molar equiv of O_2. After removal of MeCN, a solid compound was isolated which, after sublimation at 95 °C (10^{-4} Torr), yielded 610 mg (81%) of yellow crystals. Recrystallization from ether/ethanol afforded 460 mg (65%) of colorless crystals **2c**, mp 116–117 °C. ^{1}H NMR: δ 2.35 (s, 3 H), 3.64 (m, 4 H), 6.70 (m, 1 H), 7.06–7.66 (m, 4 Ar H). ^{13}C NMR: δ 21.4 (q), 39.2 (t), 41.7 (tt), 157.7 (t), 167.9 (s). IR: 2150 (–N=C), 1645 (amide I), 1554 cm^{-1} (amide II). Anal. Calcd for $C_{11}H_{12}N_2O$ (188.23): C, 70.19; H, 6.43; N, 14.89. Found: C, 70.23; H, 6.65; N, 14.88.

1-Isocyano-2-(propionylamino)ethane (2d). 5,6-Diethyl-2,3-dihydropyrazine (**1d**) (248 mg, 1.8 mmol) absorbed 1 molar equiv of O_2 within 3 h. After removal of MeCN, distillation of the residue at 83 °C (10^{-4} Torr) gave a yellow solid. Sublimation at 90 °C (10^{-4} Torr) yielded 111 mg (49%) of almost colorless crystals **2d**, mp 34–35 °C. ^{1}H NMR: δ 1.16 (t, 3 H), 2.25 (q, 2 H), 3.53 (m, 4 H), 6.25 (m, 1 H). ^{13}C NMR: δ 9.7 (q), 29.4 (t), 38.7 (t), 41.3 (tt), 157.2 (t), 174.6 (s). IR: 3307, 3075, 2984, 2150 (–N=C), 1655 (amide I), 1549 cm^{-1} (amide II). Anal. Calcd for $C_6H_{10}N_2O$ (126.16): C, 57.12; H, 7.99; N, 22.12. Found: C, 56.97; H, 7.92; N, 22.14.

1-Isocyano-2-(acetylamino)ethane (5a = 2a). The residue, obtained after 1,8-bis(acetaylamino)-3,6-diaza-4,5-dimethyl-3,5-

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octadiene (**4a**) (280 mg, 1.1 mmol) had consumed 1 molar equiv of O_2 within 11 h, was distilled at 120 °C (10^{-3} Torr). The resulting oil was separated by chromatography (silica gel, elution with ethanol/ether (1:1)). Besides 108 mg (87%) of **5a** (= **2a**, physical data, see above), 140 mg (87%) of diacetylethylenediamine (**6a**), mp 171 °C (lit.[29] mp 172 °C) were obtained.

Methyl Isocyanide (5b). 2,5-Diaza-3,4-dimethyl-2,4-hexadiene (**4b**) (80 mg, 1.0 mmol) absorbed 1 molar equiv of O_2 within 9 h. The products, methylisocyanide (**5c**) and monomethylacetamide (**6b**), were qualitatively determined by comparing their ^1H NMR spectra with those of purchased authentic material.

Phenyl Isocyanide (5c). The residue, obtained after 1,4-diaza-2,3-dimethyl-1,4-diphenyl-1,3-butadiene (**4c**) (236 mg, 1.0 mmol) had absorbed 1 molar equiv of O_2 within 14 h, was distilled at 50 °C (13 Torr). From the resulting oil, 21 mg (20%) of **5c** and 91 mg (67%) of acetanilide (**6c**), mp 84–85 °C, were obtained and identified by comparison with authentic samples.

Isocyano-(1*S*,2*S*,3*S*,5*R*)-pinan-3-ylmethane (5d). The residue, obtained after *N,N'*-bis[(1*S*,2*S*,3*S*,5*R*)-pinan-3-ylmethyl]-2,3-butanediimine (**4d**) (3.85 g, 10 mmol) had absorbed 1 molar equiv of O_2 within 4 h, afforded a yellowish oil at 87–88 °C (4×10^{-3} Torr) of **5d** (yield 1.30 g, 74%) and colorless crystals of *N*-[(1*S*,2*S*,3*S*,5*R*)-pinan-3-ylmethyl]acetamide (**6d**), mp 94–95 °C (from ether, yield 1.80 g, 87%), $[\alpha]_D^{20} = +25.4$ (ethanol, c = 5.5).

5d. ^1H NMR: δ 1.0 (s, 3 H), 1.1 (s, 3 H), 1.2 (s, 3 H), 1.5-2.5 (m, 8 H), 3.3 (m, 2 H). ^{13}C NMR: δ 21.4 (q), 22.7 (q), 28.0 (q), 31.7 (t), 33.5 (t), 36.2 (d), 38.7 (s), 40.0 (d), 41.3 (d), 47.5 (d), 48.5 (tt), 155.6 (t). IR: 2145 cm^{-1} (–N≡C). Anal. Calcd for $C_{12}H_{19}N$ (177.28): C, 81.29; H, 10.80; N, 7.90. Found: C, 81.13; H, 1072; N, 7.73.

6d. ^1H NMR: δ 1.0 (s, 3 H), 1.1 (s, 3 H), 1.2 (s, 3 H), 1.8 (m, 8 H), 2.05 (s, 3 H), 3.2 (m, 2 H), 5.7 (br, 1 H). ^{13}C NMR: δ 21.9 (q), 22.9 (q), 23.2 (q), 28.0 (q), 32.3 (t), 33.7 (t), 36.3 (d), 38.3 (s), 40.9 (d), 41.5 (d), 47.9 (d), 170.4 (s). IR: 1648, 1637 (amide I), 1565 cm^{-1} (amide II). Anal. Calcd for $C_{13}H_{23}NO$ (209.32): C, 74.59; H, 11.08; N, 6.69. Found: C, 74.55; H, 11.23; N, 6.66.

(*S*)-1-Isocyano-1-phenylethane ((*S*)-5e). The residue, obtained from 2.80 g (9.58 mmol) of (–)-*N,N'*-bis[(*S*)-1-phenylethyl]-2,3-butanediimine ((*S,S*)-**4e**) after consumption of 1 molar equiv of O_2 within 5 h, gave two fractions on distillation: a yellow oil at 35–36 °C (4×10^{-3} Torr) of (*S*)-**5e** (yield 0.94 g, 75%), $[\alpha]_D^{20} = -40.1°$ (ethanol, c = 10.25) and another yellow oil at 105–106 °C (4×10^{-3} Torr) which soon crystallized and afforded colorless crystals of *N*-[(*S*)-1-phenylethyl]acetamide ((*S*)-**6e**), mp 99–100 °C (from methanol/*n*-pentane, yield 1.28 g, 82%), $[\alpha]_D^{20} = -132.4°$ (ethanol, c = 2.35).

(*S*)-5e. ^1H NMR: δ 1.60 (d, 3 H), 4.70 (m, 1 H), 7.20 (m, 5 Ar H). ^{13}C NMR: δ 25.0 (q), 53.8 (dt, J_{CN} = 6.1 Hz), 157.0 (t, J_{CN} = 4.3 Hz). IR: 2141 (–N≡C), 759, 698 cm^{-1}. Anal. Calcd for C_9H_9N (131.17): C, 82.40; H, 6.92; N, 10.68. Found: C, 81.89; H, 6.94; N, 10.81.

(*S*)-6e. ^1H NMR: δ 1.45 (d, 3 H), 1.94 (s, 3 H), 5.10 (m, 1 H), 5.8 (br, 1 H), 7.20 (m, 5 Ar H). ^{13}C NMR: δ 21.8 (q), 23.2 (q), 48.8 (d), 169.2 (s). IR: 1642 (amide I), 1557 cm^{-1} (amide II). Anal. Calcd for $C_{10}H_{13}NO$ (163.21): C, 73.58; H, 8.03; N, 8.58. Found: C, 73.59; H, 8.06; N, 8.57.

(*R*)-1-Isocyano-1-phenylethane ((*R*)-5e). (+)-*N,N'*-bis-[(*R*)-1-phenylethyl]-2,3-butanediimine ((*R,R*)-**4e**) (2.80 g, 9.58 mmol) absorbed 1 molar equiv of O_2 within 5 h. After removal of MeCN, the residue afforded a yellowish oil at 36–37 °C (8×10^{-3} Torr) of (*R*)-**5e** (yield 0.89 g, 70%), $[\alpha]_D^{20} = +40.8°$ (ethanol, c = 12.05), and colorless crystals of *N*-[(*R*)-1-phenylethyl]acetamide ((*R*)-**6e**), mp 99–100 °C (from methanol/*n*-pentane, yield 1.24 g, 80%), $[\alpha]_D^{20} = +138.8°$ (ethanol, c = 2.35). ^1H NMR, ^{13}C NMR, and IR spectra of (*R*)-**5e** and (*R*)-**6e** are identical with those of the corresponding enantiomers.

Methyl (*S*)-2-Isocyano-3-methylbutyrate ((*S*)-5f). After consumption of 1 molar equiv of O_2 by (3*S*,8*S*)-(–)-3,8-dicarbomethoxy-4,7-diaza-2,5,6,9-tetramethyl-4,6-decadiene ((*S,S*)-**4f**) (3.12 g, 10 mmol) within 4 h, the workup procedure gave a yellowish oil at 28–29 °C (4×10^{-3} Torr) of (*S*)-**5f** (yield 550 mg, 39%), $[\alpha]_D^{20} = +4.1°$ (ethanol, c = 5.45) and colorless crystals of methyl (S)-2-acetamido-3-methylbutyrate ((*S*)-**6f**), mp 54–55 °C (from ether, yield 1.25 g, 72%), $[\alpha]_D^{20} = -28.0°$ (ethanol, c = 5.20).

(*S*)-5f. ^1H NMR: δ 1.01 (d, 3 H), 1.11 (d, 3 H), 2.30 (m, 1 H), 3.76 (s, 3 H), 4.14 (d, 1 H). ^{13}C NMR: δ 16.7 (q), 19.2 (q), 31.2 (d), 53.1 (q), 62.5 (d), 62.9 (d), 63.2 (d), 160.8 (s), 166.8 (s). IR: 2151 cm^{-1} (–N≡C). Anal. Calcd for $C_7H_{11}NO_2$ (141.17): C, 59.55; H, 7.85; N, 9.92. Found: C, 59.69, H, 7.86; N, 10.03.

(*S*)-6f. ^1H NMR: δ 0.91 (d, 3 H), 0.95 (d, 3 H), 2.04 (s, 3 H), 2.06 (m, 1 H), 3.71 (s, 3 H), 4.55 (m, 1 H), 6.04 (br, 1 H). ^{13}C NMR: δ 18.0 (q), 18.9 (q), 23.0 (q), 31.2 (d), 52.0 (q), 57.3 (q), 170.2 (s), 172.7 (s). IR: 1746, 1653 (amide I), 1541 cm^{-1} (amide II). Anal. Calcd for $C_8H_{15}NO_3$ (173.21): C, 55.47; H, 8.73; N, 8.09. Found: C, 55.83; H, 8.80; N, 8.24.

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Registry No. **1a**, 15986-92-2; **1b**, 20542-79-4; **1c**, 137465-83-9; **1d**, 73570-18-0; **1e**, 137465-84-0; **1f**, 1489-06-1; **2a**, 137465-87-3; **2b**, 137465-88-4; **2c**, 137465-89-5; **2d**, 137465-90-8; **3a**, 69849-58-7; **4a**, 137465-85-1; **4b**, 4381-85-5; **4c**, 5393-49-7; **4d**, 90495-79-7; (*S,S*)-**4e**, 67122-56-9; (*R,R*)-**4e**, 137566-61-1; (*S,S*)-**4f**, 137465-86-2; **5b**, 593-75-9; **5c**, 931-54-4; **5d**, 137465-91-9; (*S*)-**5e**, 21872-32-2; (*R*)-**5e**, 21872-33-3; (*S*)-**5f**, 63472-88-8; **6d**, 137465-92-0; (*S*)-**6e**, 19144-86-6; (*R*)-**6e**, 36283-44-0; (*S*)-**6f**, 1492-15-5; 1,2-diaminoethane, 107-15-3; 1-phenyl-1,2-propanedione, 579-07-7; 1-(4-methylphenyl)-1,2-propanedione, 1855-08-9; 3,4-hexanedione, 4437-51-8; 3-methyl-1-phenyl-1,2-butanedione, 7332-95-8; 1-(acetylamino)-2-aminoethane, 1001-53-2; diacetyl, 431-03-8; methylamine, 74-89-5; L-(+)-valine methyl ester, 4070-48-8.