N-Alkyl-5,5-dimethyl-2-oxomorpholin-3-yl Radicals. Characterization and Reaction with Molecular Oxygen

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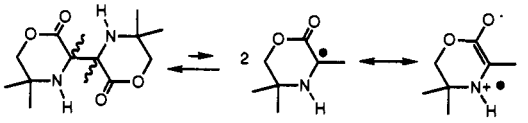
Abstract: The synthesis of bi(4,5,5-trimethyl-2-oxomorpholin-3-yl) (TM-3′ dimer), bi(5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl) (DEM-3 dimer), and bi(5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl) (DIM-3 dimer) by one-electron oxidation of 4,5,5-trimethyl-2-oxomorpholine (**8**), 5,5-dimethyl-4-ethyl-2-oxomorpholine (**9**), and 5,5-dimethyl-4-isopropyl-2-oxomorpholine (**10**), respectively, with photochemically generated *tert*-butoxyl radical is described. *dl*-TM-3′ dimer, *meso*-DEM-3 dimer, and *meso*-DIM-3 dimer were characterized from spectra and by X-ray crystallography. In solution the radical dimers existed in equilibrium with the captodatively substituted radicals, 4,5,5-trimethyl-2-oxomorpholin-3-yl (TM-3′), 5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl (DEM-3), and 5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl (DIM-3), respectively, as indicated by EPR spectroscopy. The activation parameters for bond homolysis in ethanol solvent were measured by oxidatively trapping the radicals with diphenylpicrylhydrazyl (DPPH). The half-lives for bond homolysis vary by 5 orders of magnitude at 25 °C with a value of only 2.3 s for DIM-3 dimer. DIM-3 dimer reacted quantitatively with molecular oxygen to form a mixture of *meso*- and *dl*-bis(5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl) peroxides (DIM-3 peroxides), which were isolated and characterized spectroscopically and analytically. At ambient temperature the peroxides fragmented by C–O bond homolysis to release the DIM-3 radical as indicated by EPR spectroscopy and were solvolyzed by protic solvent with release of hydrogen peroxide. The solvolysis was reversed by evaporation of the protic solvent, which restored most of the DIM-3 peroxides. The peroxides also slowly fragmented irreversibly to 5,5-dimethyl-3-hydroxy-4-isopropyl-2-oxomorpholine (**21**) and 5,5-dimethyl-2,3-dioxo-4-isopropylmorpholine (**23**) in polar aprotic solvent.

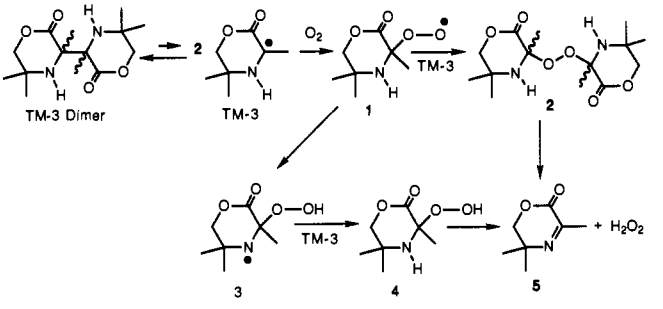
Introduction

3,5,5-Trimethyl-2-oxomorpholin-3-yl (TM-3) is a prime example within a class variously known as captodative,[1,2] merostabilized,[3] or push–pull-stabilized[4] radicals. Such radicals are ones bearing both electron-donating and electron-withdrawing substituents bonded to the radical center. The stabilization energy is being actively debated and appears to be significant for the combination of amino and carboxy substituents.[5-8] TM-3 forms upon dissolution of its radical dimers, *meso*- and *dl*-bi(3,5,5-trimethyl-2-oxomorpholin-3-yl) (*meso*- and *dl*-TM-3 dimers), at ambient temperature.[9] It exists in equilibrium with TM-3 dimers, with an equilibrium constant for radical formation varying from 10^{-11} to 10^{-16} M as a function of solvent and temperature.[10] The



TM-3 radical reacts as a mild one-electron reducing agent, most likely by electron transfer;[11,12] an exception is reduction of molecular oxygen to hydrogen peroxide, which occurs by the covalent mechanism shown in Scheme I.[13] The covalent mechanism

Scheme I



involves the combination of TM-3 with molecular oxygen to form the (3,5,5-trimethyl-2-oxomorpholin-3-yl)peroxyl radical (**1**), which either combines with a second TM-3 radical to form bis-(3,5,5-trimethyl-2-oxomorpholin-3-yl) peroxide (**2**) or intramolecularly abstracts the hydrogen atom bonded to nitrogen to form the aminyl radical, 3-hydroperoxy-3,5,5-trimethyl-2-oxomorpholin-4-yl (**3**). Subsequent reduction of the aminyl radical by TM-3 is proposed to give 3-hydroperoxy-3,5,5-trimethyl-2-oxomorpholine (**4**). Elimination of hydrogen peroxide from **2** and from **4** yields 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**5**). Of the proposed intermediates **2**, **3**, and **4**, only **3** was actually observed spectroscopically; it was characterized from its EPR spectrum when it was generated with $^{17}O_2$. Formation of the other transients was implicated from circumstantial evidence. The intermediacy of **2** is now supported from a study of *N*-alkyl-5,5-dimethyl-2-oxomorpholin-3-yl radicals. These radicals can react with molecular oxygen to form peroxides; however, the elimination of hydrogen peroxide as proposed for **2** in Scheme I is retarded by the absence of the secondary amine functionality.

The radicals designed and synthesized for this investigation relative to the TM-3 structure are missing the methyl group at the 3-position. This design feature stems from an earlier observation that the reaction of 3,4,5,5-tetramethyl-2-oxomorpholine (**6**) with di-*tert*-butyl peroxide and light yielded 3-methylidene-4,5,5-trimethyl-2-oxomorpholine (**7**) rather than the expected radical dimer.[14] The methylideneoxomorpholine **7** resulted either

(1) Viehe, H. G.; Janousek, Z.; Merĕnyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.
(2) Viehe, H. G.; Janousek, Z.; Merĕnyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *12*, 148.
(3) Baldock, R. W.; Hudson, P.; Katritzky, A. R. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1422.
(4) Balaban, A. T.; Caproiu, M. T.; Negoita, N.; Baican, R. *Tetrahedron* **1977**, *33*, 2249.
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(6) Katritzky, A. R.; Zerner, M. C.; Karelson, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 7213.
(7) Pasto, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 8164.
(8) Bordwell, F. G.; Lynch, T.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 7558.
(9) Koch, T. H.; Olesen, J. A.; DeNiro, J. *J. Am. Chem. Soc.* **1975**, *97*, 7285.
(10) Olson, J. B.; Koch, T. H. *J. Am. Chem. Soc.* **1986**, *108*, 756.
(11) Gaudiano, G.; Koch, T. H. *Chem. Res. Toxicol.* **1991**, *4*, 2.
(12) Burns, J. M.; Wharry, D. L.; Koch, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 849.
(13) Gaudiano, G.; Koch, T. H. *J. Am. Chem. Soc.* **1986**, *108*, 5014.

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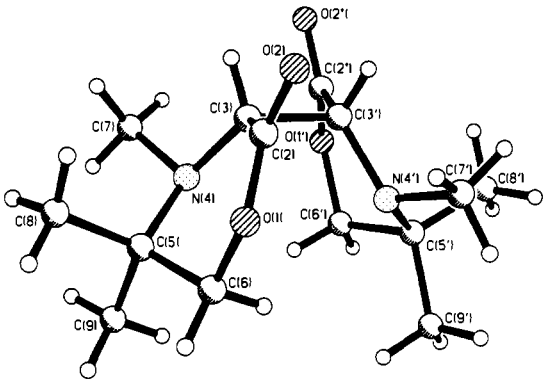


Figure 1. Perspective drawing of the *dl*-TM-3′ dimer showing the numbering scheme adopted.

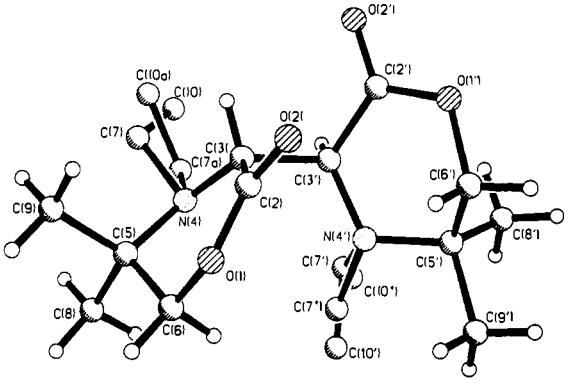
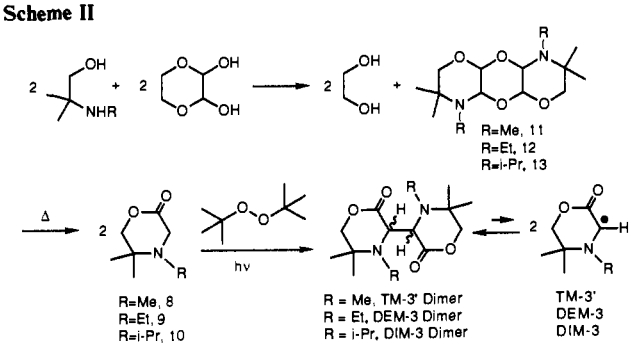
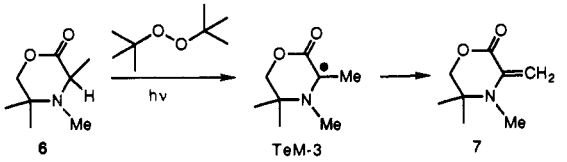


Figure 2. Perspective drawing of the *meso*-DEM-3 dimer showing the numbering scheme adopted and the disorder with respect to the *N*-ethyl substituent.

Scheme II



from *tert*-butoxyl radical oxidation of 3,4,5,5-tetramethyl-2-oxomorpholin-3-yl (TeM-3) or from disproportionation of TeM-3 in competition with dimerization.



Results and Discussion

Synthesis and Structure of *N*-Alkyl-2-oxomorpholin-3-yl Radical Dimers. The radical dimers, bi(4,5,5-trimethyl-2-oxomorpholin-3-yl) (TM-3′ dimer), bi(5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl) (DEM-3 dimer), and bi(5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl) (DIM-3 dimer), were prepared by irradiation of di-*tert*-butyl peroxide in the presence of the corresponding oxomorpholine, 4,5,5-trimethyl-2-oxomorpholine (**8**), 5,5-dimethyl-4-ethyl-2-oxomorpholine (**9**), or 5,5-dimethyl-4-isopropyl-2-oxomorpholine (**10**), respectively (Scheme II). The reaction medium was oxygen-degassed *tert*-butyl alcohol or benzene. Photolysis in *tert*-butyl alcohol gave better product yields; moreover, during the synthesis of DIM-3 dimers, the product even crystallized as the meso diastereomer from the photolysis solvent, analytically pure. Crystallization was particularly fortunate because the DIM-3 dimer was very unstable with respect to bond homolysis (vide infra). The reaction involved regioselective hydrogen atom abstraction from the 3-position of the respective oxomorpholine by *tert*-butoxyl radical. TM-3′ dimer was isolated as an approximately 1:1 mixture of meso and *dl* diastereomers, and the DEM-3 and DIM-3 dimers were isolated as meso diastereomers.

The oxomorpholines were best prepared from the respective 2-alkylamino-2-methylpropanols by condensation with 2,3-dihydroxy-1,4-dioxane to form the 4,9-dialkyl-3,3,8,8-tetramethyloctahydro-4*H*,9*H*-[1,4]dioxano[2,3-*b*:5,6-*b*′]bis[1,4]-oxazines (**11**, **12**, or **13**), followed by pyrolysis of the bisoxazines as

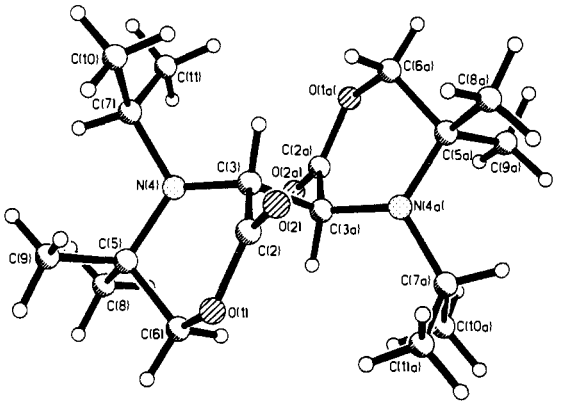


Figure 3. Perspective drawing of the *meso*-DIM-3 dimer showing the numbering scheme adopted. Atoms O(1a) to C(11a) were generated by the symmetry operator: $-x, -y, 1 - z$. Primes were not used in the numbering of *meso*-DIM-3 dimer to distinguish these symmetry atoms from the atoms in the previous structures that are not symmetry related.

described by Haas for the preparation of **11**[15] and shown in Scheme II.

The stereochemistry of the *dl*-TM-3′, *meso*-DEM-3, and *meso*-DIM-3 dimers was established by single-crystal X-ray analysis; perspective drawings are shown in Figures 1, 2, and 3. The *dl*-TM-3′ dimer showed intramolecular contact of C(2) with C(7′) and C(8) and, correspondingly, C(2′) with C(7) and C(8′). The central 3–3′ bond was 1.563 (3) Å long. The crystal of *meso*-DEM-3 dimer was disordered with respect to the ethyl groups; approximately half of the nitrogens were planar and half pyramidal with a random distribution. The DEM-3 dimer showed no significant intramolecular contacts, possibly permitting the disorder of the *N*-ethyl groups. The central 3–3′ bond was 1.569 (8) Å long. The *meso*-DIM-3 dimer showed intramolecular contact of C(3) with C(6a) and, correspondingly, C(3a) with C(6). The central 3–3a bond was 1.589 (2) Å long. The 3–3′ bonds of the *dl*-TM-3′ and *meso*-DEM-3 dimers are short relative to the 3–3′ bond of the *dl*-TM-3 dimer, which is 1.591 (4) Å long.[16] The crystal structure of the *dl*-TM-3 dimer shows significant intramolecular contact between the methyl groups at the 3- and 3′-positions;[16] these methyl groups are not present in the TM-3′, DEM-3, and DIM-3 dimers. Comparison of the torsion angle with respect to the substituents at the 3- and 3′-positions for the dimers (3a position for the DIM-3 dimer) is also of interest (vide infra): *dl*-TM-3′ dimer, 44 (2) for H–H′; *meso*-DEM-3 dimer, −67 (2) for H–H′; *meso*-DIM-3 dimer, −180 for H–H′; and *dl*-TM-3 dimer, 35 (1) for Me–Me′.[16]

Formation and Reaction of *N*-Alkyl-2-oxomorpholin-3-yl Radicals under Anaerobic Conditions. Degassed solutions of the

(14) Burns, J. M., Ph.D. Thesis, University of Colorado, Boulder, CO, 1979.

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(16) Haltiwanger, R. C.; Koch, T. H.; Olesen, J. A.; Kim, C. S.; Kim, N. K. *J. Am. Chem. Soc.* **1977**, *99*, 6327.

Table I. EPR Spectral Data

radical	temp, °C	solvent	g-value	a_H, G	a_N, G	a_{NCH_n}[a], G	a_{CH_3}, G
4,5,5-trimethyl-2-oxomorpholin-3-yl (TM-3′)	95	ethanol	2.0038	10.6	9.20	7.5	
5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl (DEM-3)	88	neat	2.0035	11.0	8.60	5.36	
	88	naphthalene	2.0035	11.1	8.60	5.40	
	81	ethanol	2.0038	10.2	9.20	5.8	
5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl (DIM-3)	72	benzene	2.0040	11.7	8.50	1.02	0.35
	20	$CHCl_3$	2.0038	10.6	8.66	1.17	0.39[b]
	64	DMSO	2.0039	10.5	8.76	1.18	0.40[c]
	72	ethanol	2.0039	10.0	9.00	1.50	0.35

[a] For each radical, n is the number of protons on the carbon of the alkyl group bonded to nitrogen. [b] A similar coupling was also observed from the ring methylene protons. [c] A 0.34 G coupling was also observed from the ring methylene protons.

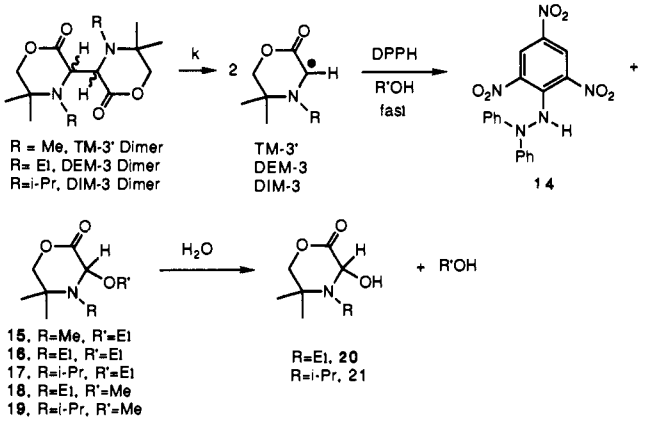
TM-3′ dimers, DEM-3 dimer, and DIM-3 dimers showed EPR spectral signals as reported in Table I for 3,5,5-trimethyl-2-oxomorpholin-3-yl (TM-3′), 5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl (DEM-3), and 5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl (DIM-3), respectively. The hyperfine coupling constants are solvent and structure dependent. Consistent with observation for related radicals, the nitrogen hyperfine coupling constant is larger in polar protic solvent;[10,17] the coupling constant for the proton at the 3-position changes inversely. A possible explanation for both is a larger resonance contribution in polar solvent from the dipolar resonance form of the captodative radicals, illustrated above for TM-3. The oxomorpholinyl radicals showed no tendency to disproportionate at ambient temperature, as indicated by long-term monitoring of anaerobic solutions of the radical dimers sealed in NMR tubes.

The rate constants and activation parameters for bond homolysis of the TM-3′, DEM-3, and DIM-3 dimers in ethanol were measured by monitoring the anaerobic reaction of the radical dimers with diphenylpicrylhydrazyl (DPPH) as a function of temperature. The reaction involves reduction of DPPH by TM-3′, DEM-3, and DIM-3 to diphenylpicrylhydrazine (**14**), which occurs faster than recombination of the oxomorpholinyl radicals. Diphenylpicrylhydrazine was characterized by chromatographic and spectroscopic comparison with a commercial sample. The products of oxidation of TM-3′, DEM-3, and DIM-3 are proposed to be 3-ethoxy-4,5,5-trimethyl-2-oxomorpholine (**15**), 5,5-dimethyl-3-ethoxy-4-ethyl-2-oxomorpholine (**16**), and 5,5-dimethyl-3-ethoxy-4-isopropyl-2-oxomorpholine (**17**), respectively. The 3-alkoxy-2-oxomorpholines were unstable with respect to isolation; however, their formation was established from clean ^{1}H NMR spectra of reaction mixture residues from solvent evaporation in deuteriochloroform, as reported in the Experimental Section. The 3-alkoxy-2-oxomorpholines underwent facile substitution by water to produce 3-hydroxy-2-oxomorpholines. The substitution was demonstrated by ^{1}H NMR spectroscopy; formation of 5,5-dimethyl-4-ethyl-3-hydroxy-2-oxomorpholine (**20**) and 5,5-dimethyl-3-hydroxy-4-isopropyl-2-oxomorpholine (**21**) was observed upon dissolving the respective reaction mixtures in a DMSO-d_6 solvent containing a trace of water. The observed splitting of the OH signal in the spectra of **20** and **21** established the secondary alcohol functional group, and the other ^{1}H NMR signals, reported in the Experimental Section, strongly indicated the proposed 3-hydroxy-2-oxomorpholine structures. Attempts to isolate and purify **20** and **21** proved unsuccessful. The oxomorpholinyl radicals react with DPPH most likely by electron transfer to form a radical ion pair, which rapidly combines with solvent to form the observed products, diphenylpicrylhydrazine and the 3-alkoxy-2-oxomorpholines (**15–19**). The reaction with DPPH was followed spectrophotometrically, monitoring disappearance of DPPH. Absorbance versus time data showed clean first-order kinetics indicating that the rate-controlling step was in fact bond homolysis of the radical dimers. The rate constants and activation parameters are reported in Table II and compared with those for the TM-3 dimer. The free energy of activation for the bond homolysis of TM-3′ dimer and DIM-3 dimer at 25 °C is 4 kcal/mol higher and 3 kcal/mol lower, respectively, than that for the bond homolysis of TM-3 dimer. These activation energies translate into 5 orders of magnitude difference in the half-lives for TM-3′ and DIM-3 dimers. Hence, the effect of a methyl group on each nitrogen versus an isopropyl group on each nitrogen translates into primarily a 7 kcal/mol steric effect on the activation energy for bond homolysis. If the predominant conformations of the TM-3′, DEM-3, and DIM-3 dimers in solution are the same as those in the solid state, then homolysis of the DIM-3 dimer might be facilitated by the 180° torsion angle about the 3–3a bond, which intuitively would permit the best orbital overlap of the incipient radical centers with the captodative substituents. Consistent with the low-energy conformation being present in the solid state is the lack of significant intermolecular contacts except for a C–H···O contact between dimers that is less than the sum of the van der Waals radii. This contact is most significant for TM-3′ dimer, 2.475 Å vs 2.72 Å for the sum of the van der Waals radii; for DEM-3 dimer, 2.67 Å; and for DIM-3 dimer, 2.59 Å. C–H···O contacts have, however, been implicated in determining molecular packing and conformation.[18]

Table II. Activation Parameters for the Bond Homolysis of Radical Dimers in Ethanol

parameter	TM-3′ dimer[a]	DEM-3 dimer[a]	TM-3 dimer[b]	DIM-3 dimer[c]
A, s^{-1}	1.2×10^{14}	4.9×10^{14}	3.1×10^{12}	1.4×10^{14}
E_a, kcal/mol	27.0 ± 0.1	25.4 ± 1.0	21.0 ± 2.0	20.0 ± 0.4
corr coeff	0.9999	0.999	0.995	0.993
$\Delta H^{\ddagger}$, kcal/mol	26.4 ± 0.1	24.8 ± 1.0	20.4 ± 2.0	19.4 ± 0.4
$\Delta S^{\ddagger}$, cal/degree·mol	4.1 ± 0.3	6.7 ± 3.3	−3.4 ± 6.4	4.2 ± 2.7
$\Delta G^{\ddagger}$, kcal/mol[d]	25.2 ± 0.2	22.8 ± 2.0	21.4 ± 3.9	18.1 ± 1.2
k^e, s^{-1}	1.9×10^{-6}	1.2×10^{-4}	1.2×10^{-3}	3.0×10^{-1}
$\tau_{1/2}$[e], s	3.6×10^{5}	5.6×10^{3}	5.8×10^{2}	2.3

[a] In 95% ethanol. [b] In absolute ethanol and taken from ref 10. [c] In 10% chloroform/90% absolute ethanol (v/v). [d] Free energy of activation at 298 K. [e] Rate constant and half-life at 298 K calculated from the Arrhenius parameters.

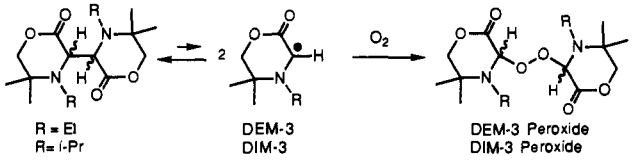


Formation and Reaction of *N*-Alkyl-2-oxomorpholin-3-yl Peroxides. In an aerobic medium, DIM-3 dimer reacted rapidly

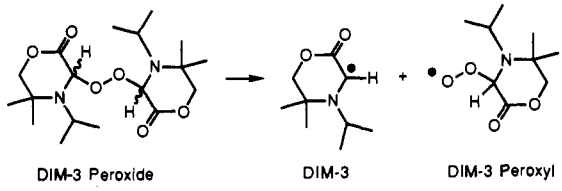
(17) Himmelsbach, R. J.; Barone, A. D.; Kleyer, D. L.; Koch, T. H. *J. Org. Chem.* **1983**, *26*, 2989.

(18) Berkovitch-Yellin, Z.; Leiserowitz, L. *Acta Crystallogr.* **1984**, *B40*, 159.

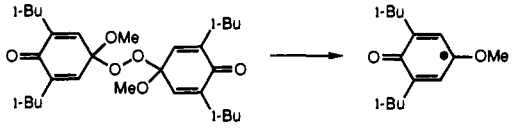
with molecular oxygen to form *meso*- and *dl*-bis(3,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl) peroxides (DIM-3 peroxides). The DIM-3 peroxides were obtained analytically pure by silica gel flash chromatography and were characterized from spectroscopic data, including a mass spectral molecular ion from negative ion chemical ionization, and complete elemental analysis including analysis for oxygen. The DEM-3 radical also formed diastereomeric peroxides upon reaction with molecular oxygen in methanol solution, as indicated by ^{1}H NMR spectroscopy; however, the peroxides were not isolated.



A weak DIM-3 EPR signal was observed at ambient temperature in ethanol with a degassed solution of chromatographically purified DIM-3 peroxides. This observation indicates facile formation of DIM-3 from C–O bond homolysis of the peroxides; (5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl)peroxyl radical (DIM-3 peroxyl) was not observed by EPR spectroscopy, possibly because it lost molecular oxygen to form the DIM-3 radical. Loss of molecular oxygen from stabilized radicals has precedence in triarylmethyl[19] and pentadienyl chemistry.[20-22] In fact, the C–O bond energy for molecular oxygen bound to stabilized radicals, such as benzyl or allyl, is estimated at only 13–15 kcal/mol.[23,24]

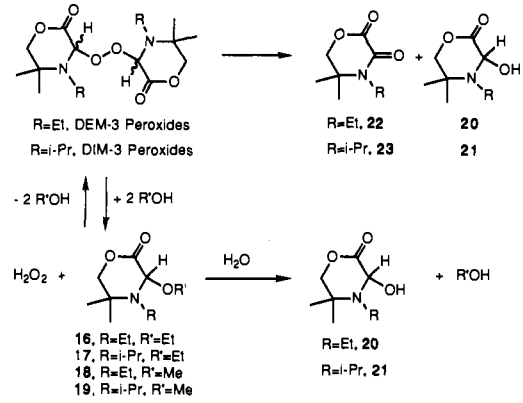


Consequently, unlike most dialkyl peroxides, DIM-3 peroxides bear weak C–O bonds, probably significantly weaker than the O–O bond. The O–O bond strength for dialkyl peroxides is in the range of 37 kcal/mol.[25] Another example of a peroxide that undergoes C–O bond homolysis to generate a captodative radical is bis(1-methoxy-3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienyl) peroxide; however, heating to 130 °C was required in this case to produce a measurable EPR signal.[26] Endoperoxides undergo both C–O and O–O bond homolysis upon heating.[27]

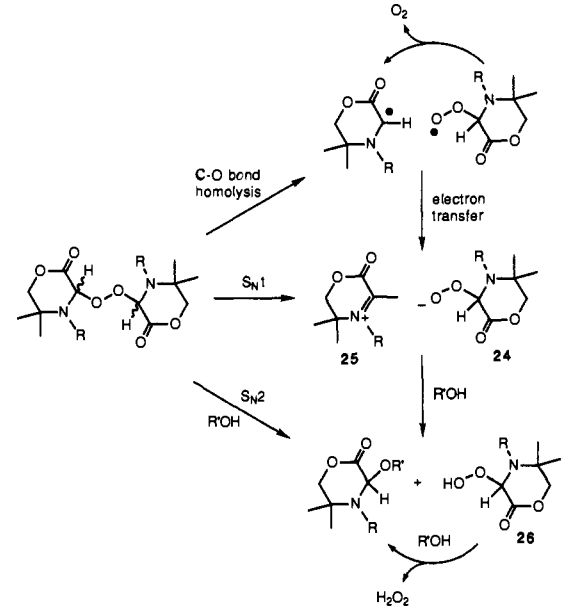


DIM-3 peroxides in DMSO-d_6 at ambient temperature in the presence or absence of molecular oxygen cleanly fragmented to an approximately 35:65 mixture of 5,5-dimethyl-2,3-dioxo-4-isopropylmorpholine (**23**) and 5,5-dimethyl-3-hydroxy-4-isopropyl-2-oxomorpholine (**21**) over a period of a day. The dioxomorpholine **23** was isolated and characterized from spectral and analytical data. As reported above, oxomorpholine **21** was unstable, but its structure was obvious from the ^{1}H NMR spectrum and the nature of the chemical reaction. DIM-3 peroxides

Scheme III



Scheme IV



also reacted with methanol at ambient temperature to yield predominantly 5,5-dimethyl-4-isopropyl-3-methoxy-2-oxomorpholine (**19**), as indicated by ^{1}H NMR spectroscopic monitoring of the reaction run in methanol-d_4 (Scheme III). Presumably hydrogen peroxide was a byproduct, consistent with the observation that evaporation of the solvent restored a major portion of the peroxide, as indicated by ^{1}H NMR analysis of the residue dissolved in $CDCl_3$ solvent. Analyzing for hydrogen peroxide by reaction with titanium tetrachloride[28] showed the presence of stoichiometric quantities. Similar reactivity occurred with DIM-3 peroxides in ethanol and DEM-3 peroxides in both methanol and ethanol solvents. Such reactivity is likely responsible for the weakness of the EPR signal observed for the DIM-3 radical present in ethanol solutions of DIM-3 peroxides (vide supra).

The peroxide chemistry appears to be dominated by ionic rather than free radical processes as best indicated by the solvolyses in protic solvent. The mechanism (Scheme IV) may be either an S_N1 process with heterolysis of a C–O bond to yield an oxomorpholinyl hydroperoxide anion (**25**) and an oxomorpholinyl cation (**24**) followed by reaction of the ion pair with solvent or a direct S_N2 displacement at the 3-position by solvent. Similarly, the oxomorpholinyl hydroperoxide (**26**) could eliminate a hydrogen peroxide anion or undergo S_N2 displacement. Formation of the ion pair could also result from C–O bond homolysis followed by electron transfer in the resulting radical pair; the DIM-3 radical was in fact observed in an ethanol solution of DIM-3 peroxides at ambient temperature. Nucleophilic substitution at the 3-position when an oxy substituent is present occurs readily, as is evident

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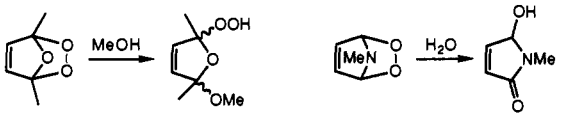
from the facile displacement of alkoxide by water in the conversion of **16** and **18** to hydroxymorpholine **20**, the conversion of **17** and **19** to hydroxymorpholine **21**, and possibly the reformation of DIM-3 peroxides from reaction of **17** and **19** with hydrogen peroxide. These latter substitutions are unlikely to occur via free radical intermediates. The irreversible fragmentation of DEM-3 peroxides to **20** and dioxomorpholine **22** and DIM-3 peroxides to **21** and dioxomorpholine **23** in DMSO may occur similarly, with reaction of the ion pair with traces of water present in the solvent. In this reaction, the oxomorpholinyl hydroperoxides must then eliminate water to form the dioxomorpholines **22** and **23**, respectively; substitution of hydroxy for hydroperoxy by water must be competitive because the ratio of **23** to **21** was 35:65 rather than 50:50.[29]

The heterolytic reactions of DEM-3 and DIM-3 peroxides are related to the facile solvolytic rearrangements of 2,5-dimethylfuran endoperoxide to 2,5-dimethyl-2-hydroperoxy-5-methoxy-2,5-dihydrofuran in methanol[30] and *N*-methylpyrrole endoperoxide to 5-hydroxy-1-methyl-Δ^3-pyrrolin-2-one in water.[31]



In summary, formation of 4-alkyl-5,5-dimethyl-2-oxomorpholin-3-yl captodative radicals via bond homolysis of their respective radical dimers is highly dependent upon the size of the substituents at the 4-position; the dimers are relatively stable with a methyl substituent and reasonably unstable with an isopropyl substituent. The resulting radicals are trapped with molecular oxygen to form peroxides that are observable and even isolable in the case of an *N*-isopropyl substituent. Consequently, the presence of an alkyl group on the nitrogen of the oxomorpholinyl radical system clearly retards peroxide decomposition. Unlike most dialkyl peroxides, including tertiary dialkyl peroxides, these appear to undergo facile heterolytic and homolytic C–O bond cleavage.

Experimental Section

General Remarks. Infrared spectra were determined with a Mattson Polaris FTIR spectrometer and UV–vis spectra with a Hewlett-Packard 8450 spectrometer. NMR spectra were obtained with a Varian EM-390 (90 MHz), Chemagnetics A200 (200 MHz), Bruker WM250 (250 MHz), or Varian VXR 300 MHz spectrometer. Chemical shifts are reported in ppm on the δ scale from internal TMS, 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt, $CHCl_3$, or C_6D_5H, and coupling constants are reported in hertz. EPR spectra were determined with a Varian 109E spectrometer; coupling constants are reported in gauss, and the *g* values were determined from a diphenylpicrylhydrazyl (DPPH) external standard. Mass spectra were obtained with a VG Instruments 7070 EQ-HF spectrometer equipped with a FAB inlet system. Gas chromatography (GC) was performed on a Varian Aerograph 1700 chromatograph equipped with a thermal conductivity detector or a Hewlett-Packard 5790A capillary chromatograph equipped with a flame ionization detector. For preparative chromatography, the Varian GC was equipped with a 0.5 cm × 185 cm column of 5% SE-30 on 60/80 mesh high-performance Cromosorb W. High-performance liquid chromatography (HPLC) was conducted on a Hewlett-Packard 1090 liquid chromatograph equipped with a diode array UV–vis detector. Photochemical reactions were performed in a Rayonet RPR 100 photochemical reactor (Southern New England Ultraviolet Co., Hamden, CT). Microanalyses were performed by Atlantic Microlab, Norcross, GA, or Galbraith Laboratories, Knoxville, TN. Flash chromatography was performed as described by Still and co-workers,[32] and dry column chromatography as described by Harwood.[33] Preparative silica gel TLC was performed with a Model 7924T Chromatotron (Harrison Research, Palo Alto, CA). Freeze–thaw degassing of samples in special spectroscopic cells was performed at (2–4) × 10^{-6} Torr as previously described.[34]

2-(Methylamino)-2-methylpropanol. Although reference to this material does appear in the literature, a detailed synthesis could not be located and, consequently, is reported here. 2-Amino-2-methylpropanol (12.1 g, 0.136 mol) was dissolved in 50 mL of 3:1 dioxane/water (v/v). The mixture was cooled to 0 °C in an ice–water bath after the addition of 0.5 g of sodium carbonate and 0.5 g of sodium bicarbonate. Di-*tert*-butyl dicarbonate (35.5 g, 0.163 mol) was added dropwise. At the conclusion of the addition, the ice bath was removed and the reaction mixture was stirred at ambient temperature for 6 h. The carbonate salts were removed by filtration, and the filtrate was extracted three times with dichloromethane. The solvents were removed by rotary evaporation at 0.1 Torr to yield 23.0 g (90%) of 2-(((*tert*-butyloxy)carbonyl)amino)-2-methylpropanol as a white solid. The material showed the following ^{1}H NMR spectrum: δ ($CDCl_3$) 1.20 (s, 6 H), 1.38 (s, 9 H), 3.54 (d, J = 6, 2 H, collapsed to a singlet with D_2O), 4.1–4.2 (broad, 2 H, disappeared with D_2O). Without further purification, 21.0 g (0.112 mol) of the *t*-BOC derivative was dissolved in 100 mL of dry tetrahydrofuran and added dropwise to a suspension of 12.5 g of lithium aluminum hydride in 200 mL of tetrahydrofuran under an atmosphere of nitrogen. At the conclusion of the addition, the reaction mixture was heated to reflux for 24 h. After the solution was cooled to ambient temperature, the excess hydride was destroyed by the dropwise addition of 15 mL of water, 15 mL of 15% sodium hydroxide, and 45 mL of water, sequentially. The reaction mixture turned white, indicating complete destruction of the excess hydride. The alkoxides were removed by suction filtration, and the solvent of the filtrate was removed by rotary evaporation to yield 10.5 g (92%) of a pale yellow liquid. The product was shown to be almost pure 2-(methylamino)-2-methylpropanol by ^{1}H NMR: δ ($CDCl_3$) 1.0 (s, 6 H), 2.24 (s, 3 H), 3.26 (s, 2 H) (the acidic proton resonances were too broad to be detected). The material was used in the synthesis of 4,5,5-trimethyl-2-oxomorpholine (**8**) without further purification. A small sample was further purified for melting point comparison by preparative gas chromatography on an SE-30 column at 65 °C eluting with helium at 60 mL/min. The resulting sample was a white crystalline solid with mp 42.5–43 °C (lit.[35] mp 41.5 °C).

4,5,5-Trimethyl-2-oxomorpholine (8). 4,5,5-Trimethyl-2-oxomorpholine (**8**) was prepared in 40% yield by condensation of 2-(methylamino)-2-methylpropanol with 2,3-dihydroxydioxane, followed by pyrolysis of the resulting 3,3,4,8,8,9-hexamethyloctahydro-4*H*,9*H*-[1,4]dioxano[2,3-*b*:5,6-*b*']bis[1,4]oxazine (**11**) as reported by Haas.[15] The procedure is described in detail below for the preparation of the analogous oxomorpholines **9** and **10**. The oxomorpholine **8** had the following spectral properties: ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 6 H), 2.21 (s, 3 H), 3.39 (s, 2 H), 4.05 (s, 2 H); IR (thin film) 2.87 (broad), 3.38, 3.60, 5.75, 6.06, 6.85, 7.35, 7.75, 7.84, 8.13, 8.89, 9.48 μm; mass spectrum (70 eV) m/z (relative intensity) 143 (M^+, 30), 128 (45), 100 (10), 85 (80), 70 (100).

Bi(4,5,5-trimethyl-2-oxomorpholin-3-yl) (TM-3′ Dimer). A 20 mm o.d. × 200 mm quartz tube was charged with 1.00 g (6.98 mmol) of 4,5,5-trimethyl-2-oxomorpholine, 0.53 g (3.6 mmol) of *tert*-butyl peroxide, and 30 mL of spectral grade benzene and equipped with a reflux condenser. The solution was oxygen degassed with argon for 10 min and irradiated for 24 h in a Rayonet reactor equipped with 16 3000-Å bulbs with continuous argon degassing. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography with a 30-mm o.d. flash column, eluting with 40% ethyl acetate/hexanes (v/v) and collecting 15-mL fractions. Removal of the solvent by rotary evaporation followed by air drying of the solid product yielded 0.314 g (32%) of bi(4,5,5-trimethyl-2-oxomorpholin-3-yl), which was a 1:1 mixture of meso and *dl* diastereomers as indicated by HPLC on a 4.6 × 240 mm C18 column eluting with 35% water/methanol (v/v) at 1.5 mL/min and detecting at 215 nm. Preparative separation of the diastereomers was accomplished by flash chromatography at 0 °C eluting with 5% acetone/dichloromethane (v/v): *dl*-TM-3′ dimer, mp 154–156 °C; *meso*-TM-3′ dimer, mp 132–134 °C. The dimers had the following spectral properties: *dl*, ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 6 H), 1.11 (s, 6 H), 2.28 (s, 6 H), 3.72 (s, 2 H), 3.85 (d, J = 10, 2 H), 4.60 (d, J = 10, 2 H); meso, ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 6 H), 1.07 (s, 6 H), 2.44 (s, 6 H), 3.71 (s, 2 H), 3.83 (d, J = 10, 2 H), 4.24 (d, J = 10, 2 H); IR ($CDCl_3$) 3.33, 5.75, 6.84, 7.25, 8.20, 9.43 μm; mass spectrum (CI, positive ion, isobutane) m/z (relative intensity) 285 ($M + H^+$, 35), 185 (10), 142 (100); UV (CH_3CN) λ_{max} 258 (ϵ 490 M^{-1} cm^{-1}). Anal. Calcd for $C_{14}H_{24}N_2O_4$: C, 59.14; H, 8.51; N, 9.85. Found: C, 59.24; H, 8.54; N, 9.80. Crystals of the *dl* isomer for X-ray crystallography were grown from 50% di-

(29) Other possible mechanisms for the fragmentation are O–O bond homolysis followed by disproportionation of the resulting oxy radical pair, base-catalyzed heterolysis of the O–O bond, and a Russell mechanism with the intermediacy of a tetraoxide (Russell, G. A. *Chem. Ind. (London)* **1956**, 1483. Howard, J. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 1056. Mendenhall, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 1656.)

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chloromethane/isooctane (v/v) by slow evaporation of the methylene chloride solvent.

The photoreaction was also conducted in *tert*-butyl alcohol. The isolated yield of a mixture of *meso*- and *dl*-TM-3′ dimers after silica gel flash chromatography eluting with chloroform at ambient temperature was 39%.

2-(Ethylamino)-2-methylpropanol. Ethyl iodide (31.2 g, 0.200 mol) was added dropwise with magnetic stirring to 17.8 g (0.200 mol) of 2-amino-2-methylpropanol. During the addition, the reaction mixture was maintained at 60–65 °C. At the conclusion of the addition, the reaction mixture was diluted with 75 mL of water, and the pH was raised to 9–10 with solid KOH. The water was rotary evaporated at ambient temperature to avoid any loss of product due to sublimation. The resulting material was vacuum sublimed at 60 °C and 0.25 Torr to yield 13.0 g (55%) of a white solid with mp 73–74 °C (lit.[36] mp 75–76 °C) and the following ^{1}H NMR spectral properties: δ ($CDCl_3$) 1.03 (s, 6 H), 1.06 (t, J = 7, 3 H), 1.6–2.1 (broad s, disappears with D_2O, 2 H), 2.51 (q, J = 7, 2 H), 3.25 (s, 2 H).

4,9-Diethyl-3,3,8,8-tetramethyloctahydro-4*H*,9*H*-[1,4]dioxano[2,3-*b*:5,6-*b*′]bis[1,4]oxazine (12). A solution of 18.0 g (0.150 mol) of 2,3-dihydroxy-1,4-dioxane in 50 mL of water was added dropwise to a solution of 17.6 g (0.150 mol) of 2-(ethylamino)-2-methylpropanol in 50 mL of water. At the conclusion of the addition, the solvent was rotary evaporated, and the remaining brown liquid was refluxed with 250 mL of ethyl acetate for 15 min. The ethyl acetate was evaporated to a volume of a few milliliters. The product precipitated upon trituration with acetone. The solid dioxanobisoxazine was collected by suction filtration and washed with cold acetone to yield 20.0 g (85% yield) of **12**. The product was pure as indicated by silica gel TLC eluting with ethyl acetate; R_f = 0.7. Material recrystallized from dimethylformamide had the following properties: mp 171–172 °C; ^{1}H NMR (D_2O) δ 1.08 (s, 3 H), 1.08 (t, X part of an ABX_3 pattern, $J_{AX} = J_{BX}$ = 7, 3 H), 1.13 (s, 3 H), 2.83 (B part of an ABX_3 pattern, J_{AB} = 15, J_{BX} = 7, 1 H), 3.27 (A part of an ABX_3 pattern, J_{AB} = 15, J_{AX} = 7, 1 H), 3.32 (d, J = 17, 1 H), 3.43 (d, J = 13, 1 H), 3.59 (d, J = 13, 1 H), 3.74 (d, J = 17, 1 H); mass spectrum (positive ion FAB, dithiothreitol-dithioerythritol matrix) m/z (relative intensity) 404 ($M^+ + 3H_2O$, 8), 351 ($M + H^+$, 26), 176 ($M/2 + H^+$, 100). Anal. Calcd for $C_{16}H_{30}N_2O_4 \cdot 2H_2O$: C, 54.9; H, 9.7; N, 8.0. Found: C, 54.9; H, 9.8; N, 8.1.

5,5-Dimethyl-4-ethyl-2-oxomorpholine (9). 4,9-Diethyl-3,3,8,8-tetramethyloctahydro-4*H*,9*H*-[1,4]dioxano[2,3-*b*:5,6-*b*′]bis[1,4]oxazine (**12**, 20.0 g, 0.0637 mol) was introduced into a round-bottom flask and pyrolyzed at 175 °C at atmospheric pressure, heating with an oil bath until the solid became liquid. The oxomorpholine was collected as a colorless liquid (16.0 g, 80%) by vacuum distillation at 65–70 °C at 0.5 Torr. Purified oxomorpholine **9** had the following spectral and chromatographic properties: ^{1}H NMR ($CDCl_3$) δ 0.99 (t, J = 7, 3 H), 1.02 (s, 6 H), 2.40 (q, J = 7, 2 H), 3.34 (s, 2 H), 3.96 (s, 2 H); IR ($CDCl_3$) 3.36, 3.54, 5.71, 6.87, 7.25, 8.16, 8.47, 8.81, 9.35, 9.52 μm; mass spectrum (EI, 70 eV) m/z (relative intensity) 157 (M^+, 48), 142 (100), 114 (10), 99 (40), 86 (55), 71 (45); silica gel TLC R_f = 0.38 (ethyl acetate), visualized with iodine. A sample was mixed with 1 equiv of picric acid in ethanol to form the picrate salt, mp 218 °C dec. Anal. Calcd for $C_{14}H_{18}N_4O_9$ (picrate): C, 43.53; H, 4.70; N, 14.50. Found: C, 43.58; H, 4.63; N, 14.52.

***meso*-Bi(5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl) (*meso*-DEM-3 Dimer).** 4-Ethyl-5,5-dimethyl-2-oxomorpholine (**9**, 3.40 g, 0.0216 mol) was added to a Pyrex tube (20 mm o.d. × 200 mm) containing 7.88 g (0.0540 mol) of *tert*-butyl peroxide in 50 mL of *tert*-butyl alcohol. The reaction mixture was degassed thoroughly by bubbling with argon and then irradiated overnight with continuous degassing with argon in a Rayonet photochemical reactor equipped with 16 3000-Å lamps. The solvent was then rotary evaporated and the product purified by silica gel flash chromatography on a column 55 mm o.d. × 70 mm, eluting with 50% ethyl acetate/hexane (v/v). Further purification was accomplished by preparative silica gel TLC with a Chromatotron eluting with 25% ethyl acetate/hexane (v/v). Pure DEM-3 dimer, meso isomer only, was obtained as 1.40 g (41%) of a white solid, mp 83–84 °C, which had the following spectral and chromatographic properties: ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 6 H), 1.10 (s, 6 H), 1.13 (t, X part of an ABX_3 pattern, $J_{AX} = J_{BX}$ = 7, 6 H), 2.80 (A part of an ABX_3 pattern, J_{AB} = 15, J_{AX} = 7, 2 H), 3.01 (B part of an ABX_3 pattern, J_{AB} = 15, J_{BX} = 7, 2 H), 3.76 (d, J = 11, 2 H), 3.94 (s, 2 H), 4.31 (d, J = 11, 2 H); IR ($CDCl_3$) 3.34, 5.76, 6.80, 7.25, 7.75, 8.20, 9.43 μm; mass spectrum (CI, positive ion, isobutane) m/z (relative intensity) 156 ($M^+/2$, 100), 126 (31), 100 (15), 70 (28); UV (CH_3CN) λ_{sh} 250 (ϵ 480 M^{-1} cm^{-1}); silica gel TLC, R_f = 0.40 (40% ethyl acetate/hexanes (v/v)), visualized with 3% ninhydrin in butanol. Anal. Calcd for $C_{16}H_{28}N_2O_4$: C, 61.51; H, 9.03; N, 8.97. Found: C, 61.49; H, 9.03; N, 8.95. Crystals for X-ray crystallography were obtained from 10% ethyl acetate/hexane (v/v).

2-(Isopropylamino)-2-methylpropanol. Isopropyl iodide (42.5 g, 0.250 mol) was added dropwise with magnetic stirring to 44.5 g (0.500 mol) of 2-amino-2-methylpropanol. During the addition, the reaction mixture was maintained at 60–65 °C. At the conclusion of the addition, the reaction mixture was extracted with chloroform. The chloroform was rotary evaporated, and the residue solidified upon cooling. The crude solid was recrystallized from petroleum ether to yield 8.0 g (24%) of 2-(isopropylamino)-2-methylpropanol as a white solid with mp 43–45 °C (lit.[36] mp 43–45 °C) and the following ^{1}H NMR spectral properties: δ ($CDCl_3$) 1.07 (s, 6 H), 1.06 (d, J = 6, 6 H), 1.6–2.1 (broad s, 2 H, disappears with D_2O), 2.93 (sept, J = 6, 1 H), 3.23 (s, 2 H).

4,9-Diisopropyl-3,3,8,8-tetramethyloctahydro-4*H*,9*H*-[1,4]dioxano-[2,3-*b*:5,6-*b*′]bis[1,4]oxazine (13). A solution of 7.2 g (0.060 mol) of 2,3-dihydroxy-1,4-dioxane in 50 mL of water was added dropwise to a solution of 7.9 g (0.060 mol) of 2-(isopropylamino)-2-methylpropanol in 50 mL of water. The reaction mixture was stirred overnight and then heated to 70–80 °C for 2 h. The solvent was rotary evaporated, and the solid dioxanobisoxazine was collected by suction filtration and washed with cold dimethylformamide. The solid obtained was recrystallized from DMF to yield 9.0 g of **13** (88% yield). The recrystallized product had the following properties: mp 135 °C; ^{1}H NMR (D_2O) δ 1.05 (d, J = 8, 6 H), 1.08 (s, 6 H), 3.36 (d, J = 13, 1 H), 3.40 (s, 2 H), 3.64 (d, J = 13, 1 H), 3.76 (sept, J = 8, 1 H); mass spectrum (positive ion FAB, dithiothreitol–dithioerythritol matrix) m/z (relative intensity) 432 ($M^+ + 3H_2O$, 3), 379 ($M + H^+$, 15), 190 ($M/2 + H^+$, 100). Anal. Calcd for $C_{18}H_{34}N_2O_4 \cdot 2H_2O$: C, 57.1; H, 10.1; N, 7.4. Found: C, 57.1; H, 10.1; N, 7.5.

5,5-Dimethyl-4-isopropyl-2-oxomorpholine (10). 4,9-Diisopropyl-3,3,8,8-tetramethyloctahydro-4*H*,9*H*-[1,4]dioxano[2,3-*b*:5,6-*b*′]bis[1,4]-oxazine (**13**, 16.3 g, 0.0477 mol) was introduced into a round-bottom flask and pyrolyzed at atmospheric pressure, heating with an oil bath until the solid became liquid (145–150 °C). Oxomorpholine **10** was collected as a colorless liquid (13.0 g, 80%) by vacuum distillation at 75–80 °C at 0.1 Torr. The purified material had the following spectral and chromatographic properties: ^{1}H NMR ($CDCl_3$) δ 1.02 (d, J = 7, 6 H), 1.15 (s, 6 H), 3.33 (sept, J = 7, 1 H), 3.51 (s, 2 H), 3.96 (s, 2 H); mass spectrum (EI, 70 eV) m/z (relative intensity) 171 (M^+, 42), 156 (100), 144 (10), 128 (12), 114 (40), 98 (25), 86 (32), 70 (90); mass spectrum exact mass m/z 171.1259 (calcd 171.1255); silica gel TLC R_f = 0.42 (30% ethyl acetate/hexanes, v/v), visualized with iodine. Combustion analysis was performed on the picrate salt recrystallized from ethanol, mp 186 °C dec. Anal. Calcd for $C_{15}H_{20}N_4O_9$: C, 45.00; H, 5.04; N, 14.00. Found: C, 45.04; H, 4.99; N, 14.00.

Bi(5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl) (DIM-3 Dimer). 4-Isopropyl-5,5-dimethyl-2-oxomorpholine (**10**, 3.80 g, 0.0222 mol) was added to a Pyrex tube (2 × 20 cm) containing 8.10 g (0.0555 mol) of *tert*-butyl peroxide in 50 mL of *tert*-butyl alcohol. The reaction mixture was degassed thoroughly by bubbling with argon and then irradiated overnight in a Rayonet photochemical reactor equipped with 3000-Å lamps with continuous argon degassing. A white solid crystallized during the photoreaction that was collected by suction filtration to yield 2.4 g (63%) of analytically pure DIM-3 dimer, mp 120–130 dec. Some of the crystals were of suitable quality for X-ray crystallography; the sample had the meso configuration. The photochemical reaction was also conducted on a small scale (0.380 g of **10**, 0.486 g of di-*tert*-butyl peroxide, and 2.4 mL of *tert*-butyl alcohol) with freeze–pump–thaw degassing and sealing with a torch. The yield of solid DIM-3 dimer was 0.31 g (82%). The ^{1}H NMR spectrum of DIM-3 dimer dissolved in $CDCl_3$ showed both diastereomers, as well as both diastereomers of bis(5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl) peroxide. Consequently, the sample for the NMR analysis of DIM-3 dimer was prepared in freeze–pump–thaw degassed $CDCl_3$ solvent with degassing of the solvent before mixing with the solid DIM-3 dimer under high vacuum. The sample was then sealed with a torch. The ^{1}H NMR spectrum showed both stereoisomers in a 35% to 65% ratio as follows: (major isomer) δ 0.98 (d, J = 7, 6 H), 1.04 (d, J = 7, 6 H), 1.18 (s, 6 H), 1.22 (s, 6 H), 3.24 (sept, J = 7, 2 H), 3.70 (s, 2 H), 3.88 (d, J = 11, 2 H), 4.42 (d, J = 11, 2 H); (minor isomer) δ 1.05 (d, J = 7, 6 H), 1.12 (s, 6 H), 1.13 (s, 6 H), 1.22 (d, J = 7, 6 H), 3.28 (sept, J = 7, 2 H), 3.76 (d, J = 11, 2 H), 3.85 (s, 2 H), 4.25 (d, J = 11, 2 H); mass spectrum (CI, isobutane, positive ion) m/z (relative intensity) 340 (M^+, 1), 171 (65), 170 ($M^+/2$, 100), 140 (20), 98 (12), 70 (22). Anal. Calcd for $C_{18}H_{32}N_2O_4$: C, 63.53; H, 9.41; N, 8.24. Found: C, 63.41; H, 9.44; N, 8.28.

Bis(5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl) Peroxide (DIM-3 Peroxide). Bi(5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl) was dissolved in dimethyl sulfoxide, chloroform, methanol, or ethanol in the presence of molecular oxygen. The solvent was rotary evaporated to give in excess of 90% yield of the diastereomers of DIM-3 peroxide as indicated by ^{1}H NMR spectroscopy. DIM-3 peroxide was further purified

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by preparative silica gel TLC on a Chromatotron eluting with 50% ethyl acetate/hexane (v/v). The diastereomeric mixture of DIM-3 peroxides (70% recovery) was obtained as a white solid with the following properties: mp 114–117 °C with gas evolution; ^{1}H NMR major isomer (60%) (C_6D_6) δ 0.63 (s, 6 H), 0.71 (s, 6 H), 0.78 (d, J = 7, 6 H), 1.14 (d, J = 7, 6 H), 2.71 (sept, J = 7, 2 H), 3.43 (d, J = 11, 2 H), 4.77 (d, J = 11, 2 H), 5.57 (s, 2 H), ($CDCl_3$) δ 1.06 (d, J = 7, 6 H), 1.09 (d, J = 7, 6 H), 1.13 (s, 6 H), 1.15 (s, 6 H), 3.26 (sept, J = 7, 2 H), 3.43 (d, J = 12, 2 H), 4.64 (d, J = 12, 2 H), 5.18 (s, 2 H), minor isomer (40%) (C_6D_6) δ 0.64 (s, 6 H), 0.71 (s, 6 H), 0.77 (d, J = 7, 6 H), 1.10 (d, J = 7, 6 H), 2.71 (sept, J = 7, 2 H), 3.42 (d, J = 11, 2 H), 4.71 (d, J = 11, 2 H), 5.69 (s, 2 H), ($CDCl_3$) δ 1.06 (d, J = 7, 6 H), 1.09 (d, J = 7, 6 H), 1.14 (s, 6 H), 1.16 (s, 6 H), 3.27 (sept, J = 7, 2 H), 3.83 (d, J = 12, 2 H), 4.57 (d, J = 12, 2 H), 5.27 (s, 2 H); IR (Nujol) 5.69, 7.07, 7.27, 7.55, 8.0, 8.47, 9.52, 10.99, 11.49, 13.33 μm; mass spectrum (CI, negative ion, isobutane) m/z (relative intensity) 372 (M^-, 100), 230 (40), 158 (10), 89 (10); UV (CH_3CN) λ_{max} 238 (ϵ 5200 M^{-1} cm^{-1}). Anal. Calcd for $C_{18}H_{32}N_2O_6$: C, 58.05; H, 8.66; N, 7.52; O, 25.77. Found: C, 57.86; H, 8.87; N, 7.42; O, 25.30.

Kinetics of Bond Homolysis of Radical Dimers. In a typical experiment, 2.42 mg (6.13×10^{-3} mmol) of diphenylpicrylhydrazyl (DPPH) was dissolved in 50 mL of 95% ethanol degassed with nitrogen. The radical dimer (3.5×10^{-3} mmol) was dissolved in 25 mL of spectrograde methylene chloride. A syringe was used to transfer 0.60 mL (0.80×10^{-4} mmol) of the radical dimer solution into the spectral cell compartment of a two-compartment cell. The dichloromethane was evaporated with a stream of nitrogen before 3.0 mL (3.92×10^{-4} mmol) of the DPPH solution was injected into the second compartment. The ethanol solution was freeze–thaw degassed and sealed with a torch. After 7 min for temperature equilibration in a thermostated cell holder, the DPPH solution was vigorously mixed with the dimer, and the average absorbance from 516–520 or 550–570 nm was monitored as a function of time. Rate constants and activation parameters were determined by using standard methodology. Because the DIM-3 dimer was not very soluble in ethanol and dissolved slowly, it was predissolved in a small amount of degassed chloroform prior to mixing with a freeze–thaw degassed absolute ethanol solution of DPPH. The manipulations were conducted in a three-compartment cell, and the resulting solvent was 10% chloroform/90% ethanol (v/v).

Reaction of *meso*-Bi(5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl) (DEM-3 Dimer) with 2,2-Diphenyl-1-picrylhydrazyl (DPPH). 2,2-Diphenyl-1-picrylhydrazyl hydrate (DPPH·hydrate) (0.208 g, 0.528 mmol) was dissolved in 300 mL of reagent grade methanol. The solution was deoxygenated by bubbling nitrogen into the solution for 45 min. Then, 15 mL of a methanolic solution of 0.082 g (0.264 mmol) of *meso*-bi-(5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl) was introduced through a syringe into the deoxygenated solution. The reaction mixture was heated to 50 °C in an oil bath for 20 min, during which time the color of the solution turned brown. The solvent was then rotary evaporated. The ^{1}H NMR spectrum in $CDCl_3$ of the residue after solvent evaporation showed the presence of 2,2-diphenylpicrylhydrazine (**14**), 5,5-dimethyl-4-ethyl-3-methoxy-2-oxomorpholine (**18**), and 5,5-dimethyl-4-ethyl-3-hydroxy-2-oxomorpholine (**20**), with the oxomorpholines in an approximately 3:1 ratio. The spectral patterns for **18** and **20** were as follows: **18**, ^{1}H NMR δ 1.12 (t, J = 8, 3 H, X_3 portion of ABX_3 pattern), 1.16 (s, 6 H), 2.75–2.89 (m, B portion of ABX_3 pattern), 2.9–3.05 (m, A portion of ABX_3 pattern), 3.36 (s, 3 H), 3.90 (d, J = 11, 1 H), 4.43 (s, 1 H), 4.53 (d, J = 11, 1 H), **20**, the ABX_3 pattern overlapped with that of **18**, the other patterns appeared at δ 1.20 (s, 3 H), 1.25 (s, 3 H), 3.97 (d, J = 11, 1 H), 4.50 (d, J = 11, 1 H), 4.97 (s, 1 H). Upon addition of D_2O, the ratio of **18** to **20** decreased to approximately 3:2. The ^{1}H NMR spectrum of the reaction mixture in DMSO-d_6 showed the spectrum of 2,2-diphenyl-1-picrylhydrazine and that assigned to 5,5-dimethyl-4-ethyl-3-hydroxy-2-oxomorpholine (**20**): δ 1.00 (t, X part of an ABX_3 pattern, $J_{AX} = J_{BX}$ = 8, 3 H), 1.05 (s, 3 H), 1.10 (s, 3 H), 2.70 (A part of an ABX_3 pattern, J_{AB} = 14, J_{AX} = 8, 1 H), 2.80 (B part of an ABX_3 pattern, J_{AB} = 14, J_{BX} = 8, 1 H), 3.96 (d, J = 12, 1 H), 4.43 (d, J = 12, 1 H), 4.71 (d, J = 4, 1 H), 6.23 (d, J = 4, 1 H). Moreover, when a drop of D_2O was added, the peak at δ 4.71 collapsed to a singlet and the peak at δ 6.23 disappeared. 2,2-Diphenyl-1-picrylhydrazine was isolated in quantitative yield by silica gel flash chromatography eluting with ethyl acetate. The ^{1}H NMR in $CDCl_3$ of 2,2-diphenyl-1-picrylhydrazine was identical with that of an authentic sample obtained from Aldrich. The oxomorpholines **18** and **20** were unstable with respect to many attempts to isolate them.

Reaction of *meso*-Bi(5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl) (*meso*-DEM-3 Dimer) with Oxygen To Form Peroxides. Oxygen gas was bubbled into a methanolic solution prepared by dissolving 0.312 g (1.00 mmol) of *meso*-bi(5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl) in 20 mL of spectral grade methanol. After 2 h a sample was removed, the solvent rotary evaporated, and the ^{1}H NMR spectrum observed in $CDCl_3$ solvent. The spectrum showed a mixture of two diastereomers of bis(5,5-dimethyl-4-ethyl-2-oxomorpholin-3-yl) peroxide (DEM-3 peroxides, 31% and 40%) and *meso*-DEM-3 dimer (29%). The resolved downfield signals that indicated the formation of the peroxides were as follows: ^{1}H NMR major isomer δ 3.90 (d, J = 11, 2 H), 4.56 (d, J = 11, 2 H), 5.08 (s, 2 H), minor isomer, δ 3.87 (d, J = 11, 2 H), 4.51 (d, J = 11, 2 H), 5.16 (s, 2 H). Signals consistent with the peroxide structure also appeared in the regions δ 1.1 and δ 2.75–3.1 for the methyl groups and the methylenes of the ethyl groups; these overlapped with the corresponding signals for the *meso*-DEM-3 dimer. After a total of 3 h, the solvent was removed from the reaction mixture by rotary evaporation, and the crude product was purified by silica gel TLC with a Chromatotron eluting with chloroform. Two major products were detected. The product with R_f = 0.5 was isolated as a white solid (0.073 g, 43%), characterized as 5,5-dimethyl-4-ethyl-2,3-dioxomorpholine (**22**) from the following properties: mp 90 °C; ^{1}H NMR δ ($CDCl_3$) 1.15 (t, J = 7, 3 H), 1.40 (s, 6 H), 3.46 (q, J = 7, 2 H), 4.21 (s, 2 H); mass spectrum (EI, 70 eV) m/z (relative intensity) 171 (M^+, 25), 128 (20), 114 (15), 100 (10), 86 (15), 70 (25), 56 (100). Anal. Calcd for $C_8H_{13}NO_3$: C, 56.1; H, 7.6; N, 8.2. Found: C, 55.98; H, 7.73; N, 8.09. The other product, with R_f = 0.8, characterized as 5,5-dimethyl-4-ethyl-3-hydroxy-2-oxomorpholine (**20**), was obtained as a liquid (0.070 g, 41%), which had an ^{1}H NMR spectrum identical with the spectrum of **20** described above from reaction of DEM-3 dimer with DPPH. The ^{1}H NMR spectrum showed the material to be approximately 70% pure; as reported above, **20** was unstable to various methods for further purification.

Fragmentation of Bis(5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl) Peroxide (DIM-3 Peroxides). DIM-3 peroxides were dissolved in DMSO-d_6, and the solution was monitored by ^{1}H NMR spectroscopy over a period of a day. During this time, the peroxides fragmented quantitatively to an approximately 35:65 mixture of 5,5-dimethyl-2,3-dioxo-4-isopropylmorpholine (**23**) and 5,5-dimethyl-3-hydroxy-4-isopropyl-2-oxomorpholine (**21**). The DMSO was rotary evaporated under high vacuum (0.1 Torr) and the resulting material flash chromatographed on silica gel eluting with 20% ethyl acetate/dichloromethane (v/v). The only material that cleanly eluted from the column was the dioxomorpholine **23**, which was obtained as a white solid with the following properties: mp 122 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 6 H), 1.46 (d, J = 7, 6 H), 3.60 (sept, J = 7, 1 H), 4.16 (s, 2 H); mass spectrum (EI, 70 eV) m/z 185 (M^+, 25), 130 (30), 56 (100); mass spectrum (CI, positive ion, methane) m/z 186 ($M + H^+$). Anal. Calcd for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.19; H, 8.21; N, 7.48. All attempts to isolate the hydroxyoxomorpholine **21** failed; however, the clean ^{1}H NMR spectrum of the 35:65 mixture of **23** and **21** in DMSO-d_6 established its structure: δ 0.94 (d, J = 7, 3 H), 1.02 (s, 3 H), 1.04 (d, J = 7, 3 H), 1.12 (s, 3 H), 3.30 (sept, J = 7, 1 H), 3.92 (d, J = 12, 1 H), 4.52 (d, J = 12, 1 H), 4.82 (d, J = 5, 1 H), 5.96 (d, J = 5, 1 H), the doublet at δ 5.96 disappeared and the doublet at δ 4.82 collapsed to a singlet upon addition of a drop of D_2O.

The same cleavage reaction was observed in a similar DMSO-d_6 solution of DIM-3 peroxides, freeze–thaw degassed and sealed with a torch in an NMR tube.

Reaction of Bi(5,5-dimethyl-4-isopropyl-2-oxomorpholin-3-yl) (DIM-3 Dimer) with 2,2-Diphenyl-1-picrylhydrazyl (DPPH). One compartment of a two-compartment reaction vessel was charged with a solution of 0.0241 g (6.12×10^{-5} mol) of 2,2-diphenylpicrylhydrazyl hydrate (DPPH·H_2O) in 30 mL of spectral grade methanol, and the other compartment was charged with 0.0104 g (3.06×10^{-5} mol) of solid DIM-3 dimer. The methanol solution was freeze–thaw degassed through three cycles, and then the apparatus was sealed at 5×10^{-6} Torr with a torch. The DIM-3 dimer was added to the methanol solution, and the reaction mixture was allowed to stand at ambient temperature overnight. The long reaction time was employed to compensate for the slow rate of dissolution of DIM-3 dimer in pure methanol. Occurrence of reaction was evident from the change in color from pink to brown, the color of 2,2-diphenylpicrylhydrazine. The vessel was broken open and the solvent was removed by rotary evaporation. The ^{1}H NMR spectrum of the reaction mixture in $CDCl_3$ showed only two products, diphenylpicrylhydrazine (**14**) and 5,5-dimethyl-4-isopropyl-3-methoxy-2-oxomorpholine (**19**). The diphenylpicrylhydrazine was identified by comparison of the NMR spectrum with that of an authentic sample and the oxomorpholine **19** from the following spectral patterns: ^{1}H NMR δ 1.05 (d, J = 7, 3 H), 1.13 (d, J = 7, 3 H), 1.15 (s, 3 H), 1.17 (s, 3 H), 3.29 (sept, J = 7, 1 H), 3.30 (s, 3 H), 3.84 (d, J = 11, 1 H), 4.47 (s, 1 H), 4.58 (d, J = 11, 1 H). When the reaction was similarly performed in absolute ethanol, the ^{1}H NMR spectrum of the residue from solvent evaporation showed formation of both diphenylpicrylhydrazine and 5,5-dimethyl-4-isopropyl-3-ethoxy-2-oxomorpholine (**17**). The spectrum of oxomorpholine **17** in $CDCl_3$ was as follows: ^{1}H NMR δ 1.07 (d, J = 7, 3

H), 1.15 (d, J = 7, 3 H), 1.16 (s, 3 H), 1.19 (s, 3 H), 1.19 (t, J = 7, 3 H), 3.28 (sept, J = 7, 1 H), 3.51 (q, J = 7, 2 H), 3.83 (d, J = 12, 1 H), 4.56 (s, 1 H), 4.65 (d, J = 12, 1 H), and in DMSO-d_6 δ 1.01 (d, J = 7, 3 H), 1.06 (d, J = 7, 3 H), 1.11 (d, J = 7, 3 H), 1.12 (s, 3 H), 1.13 (s, 3 H), 3.34 (sept, J = 7, 1 H), 3.42 (q, J = 7, 2 H), 3.96 (d, J = 11, 1 H), 4.41 (d, J = 11, 1 H), 4.48 (s, 1 H). Upon addition of D_2O to the sample in DMSO-d_6, some of **17** was converted to 5,5-dimethyl-4-isopropyl-3-hydroxy-2-oxomorpholine (**21**), as indicated by comparison of the ^1H NMR spectral patterns with those described for **21** above.

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Registry No. 8, 136476-52-3; **9**, 136476-53-4; **10**, 136476-54-5; **12**, 136503-80-5; **13**, 136503-81-6; **17**, 136476-61-4; **18**, 136476-60-3; **19**, 136476-59-0; **20**, 136476-57-8; **21**, 136476-58-9; **22**, 136476-55-6; **23**, 136476-56-7; *dl*-TM-3′ dimer, 136476-50-1; *meso*-TM-3′ dimer, 136476-51-2; *meso*-DEM-3 dimer, 136476-49-8; *dl*-DIM-3 dimer, 136476-48-7; *meso*-DIM-3 dimer, 136476-47-6; *dl*-DIM-3 peroxide, 136476-46-5; *meso*-DIM-3 peroxide, 136476-45-4; *dl*-DEM-3 peroxide, 136476-44-3; *meso*-DEM-3 peroxide, 136503-79-2; DPPH, 1898-66-4; 2-(methylamino)-2-methylpropanol, 27646-80-6; 2-amino-2-methylpropanol, 124-68-5; 2-(((*tert*-butyloxy)carbonyl)amino)-2-methylpropanol, 102520-97-8; 2-(ethylamino)-2-methylpropanol, 82922-13-2; 2-(isopropylamino)-2-methylpropanol, 90434-44-9.

Supplementary Material Available: A complete description of the X-ray crystallographic determinations of *dl*-TM-3′, *meso*-DEM-3, and *meso*-DIM-3 dimers, including tables of atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths, and bond and torsion angles (26 pages); listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

Photophysical Properties of C_{70}

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Abstract: Several important photophysical properties of the fullerene C_{70} have been determined. Fluorescence is weak but measurable. The yields of triplet C_{70} and of singlet oxygen are high, but not quite quantitative; the triplet energy is slightly above 33 kcal/mol. The triplet has an absorption spectrum that resembles that of C_{60} in some respects but is somewhat stronger and lacks a strong red-infrared absorption present in the C_{60} spectrum. Overall, the behavior of C_{70} is similar to that of C_{60}, but the lower symmetry relaxes the forbiddenness of some absorption and emission processes.

Introduction

Preparation and purification of the surprisingly stable spheroidal carbon molecules ("fullerenes") C_{60} and C_{70}[1-5] have created a massive effort to determine the properties of these new molecules.[6-10] We have reported many photophysical properties of C_{60},[6] some of which have recently been confirmed.[7,8] In particular, C_{60} gives a nearly quantitative yield of triplet and singlet oxygen. We now report that C_{70} has photophysical properties that resemble those of C_{60} but differ in important respects.

Experimental Section

Materials. Benzene (Fisher Spectranalyzed) was purified by washing with H_2SO_4, followed by distillation from LAH. Benzonitrile (Eastman) was purified by washing with K_2CO_3, followed by distillation from P_2O_5. Deuterated benzene (Cambridge Isotope Laboratories), hexanes (Fisher Spectranalyzed), 3-methylpentane (Aldrich), and methylcyclohexane (Aldrich Gold Label) were used as received. Anthracene (MC&B) was purified by recrystallization from acetone, and acridine (Aldrich) from toluene. Tetraphenylporphine (TPP), rubrene (Aldrich), and tetracene (Aldrich) were used as received. C_{60} and C_{70} were prepared and purified by the previously reported method.[5,9]

Steady-State Spectroscopy. Steady-state emission spectra were recorded on a SPEX Fluorolog 2 fluorimeter, equipped with a Hamamatsu R928 photomultiplier tube (PMT). All solutions were analyzed in a 1-cm^2 cell, and oxygen was removed by purging with argon (Liquid Air, >99.99% purity) for 25 min when necessary. The approximate fluorescence yield was estimated by comparing the fluorescence intensities of C_{70} and tetracene, with use of identical optical densities at the excitation wavelength (469 nm).

$^1O_2$ Quantum Yields. The apparatus was a modification of the one previously described.[11] C_{70} was excited at 532 and 355 nm by using the second and third harmonic, respectively, of a Quanta-Ray DCR-2 Nd:YAG laser, with pulse energies of 1-3.5 mJ/pulse; the dependence of the signal on energy is linear in this region. The laser pulse was filtered to remove any fundamental with a 355/532 nm pass-1060 nm reflecting mirror (Newport Corp.), followed with a KG-3 (Schott Glass) infrared absorbing filter. The 355-nm pulse was also filtered with a 355 nm

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