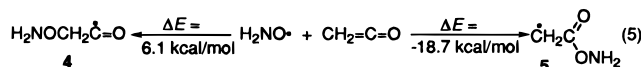
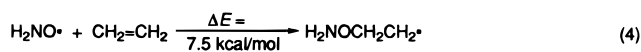


in that attack at C_β of ketene is favored kinetically, even though in the case of CH_3 and groups containing lone pairs of electrons (OH, F, Cl) the enolic radicals **2** from attack at C_α are predicted to be more stable. Therefore we were interested in finding suitable methods for studying free radical reactions of ketenes in solution and required convenient sources of free radicals such that the radical precursors and their means of generation did not themselves cause interfering side reactions of the ketenes.

Results and Discussion

Our previous theoretical studies^{3c} show that density functional theory using the B3LYP functional gives good agreement with available experimental data for eq 1, and this method has also been extensively used in calculations of nitroxyl radicals.^{3d} Therefore, as a means of assessing the feasibility of the reaction of nitroxyl radicals with ketenes, we have carried out B3LYP/6-31G*/B3LYP/6-31G* calculations, implemented with Gaussian 94,^{5a} for addition of the prototypical nitroxyl radical $\text{H}_2\text{NO}^\bullet$ to $\text{CH}_2=\text{CH}_2$, forming $\text{H}_2\text{NOCH}_2\text{CH}_2^\bullet$, and to $\text{CH}_2=\text{C}=\text{O}$, forming $\text{H}_2\text{NOCH}_2\text{C}(\bullet)=\text{O}$ (**4**) or $^\bullet\text{CH}_2\text{CO}_2\text{NH}_2$ (**5**). These calculations predict the former reactions to be endothermic, by 7.5 and 6.1 kcal/mol, respectively (eqs 4 and 5).^{5b} However,



attack at the carbonyl carbon of $\text{CH}_2=\text{C}=\text{O}$ forming $^\bullet\text{CH}_2\text{CO}_2\text{NH}_2$ is predicted to be exothermic by 18.7 kcal/mol.^{5b} Details of the calculated structures are given in the Supporting Information. By comparison, addition of HO^\bullet to the carbonyl carbon of $\text{CH}_2=\text{C}=\text{O}$ was calculated^{3c} to be exothermic by 54.7 kcal/mol.

The structures of adducts **4** and **5**^{5b} resemble the corresponding HO^\bullet adducts **1** and **2**, but the formation of the latter was more exothermic than formation of **4** and **5** by 38.7 and 36.0 kcal/mol, respectively. The acyl radical **4** has a syn coplanar arrangement of the $\text{O}-\text{C}=\text{O}$ bonds, while the enolic radical **5** is planar with the spin concentrated on C_β and has a significant degree of $\text{C}-\text{C}$ single-bond character, with a bond length of 1.443 Å. A similar situation is found in other enolic radicals **2**, where the group R has lone pairs of electrons capable of delocalization with the carbonyl group.^{3c}

As a test of the predicted feasibility of attachment of nitroxyl radicals to the carbonyl carbon of ketene and to explore the reactivity of nitroxyl radicals, the reaction of TEMPO with $\text{Ph}_2\text{C}=\text{C}=\text{O}$ was examined. This ketene is more reactive than $\text{CH}_2=\text{C}=\text{O}$ toward H_2O by a factor of 8.0,^{3a} and this greater reactivity has been attributed^{3a} to delocalization of the developing charge by the aryl groups in a transition state with some zwitterionic character, which more than overcomes the steric hindrance by the phenyl groups to in-plane nucleophilic attack by H_2O on the carbonyl carbon. Mixing of $\text{Ph}_2\text{C}=\text{C}=\text{O}$ with TEMPO in CDCl_3 at room temperature led to disappearance of the ketene within 2 h and formation of an oil which was

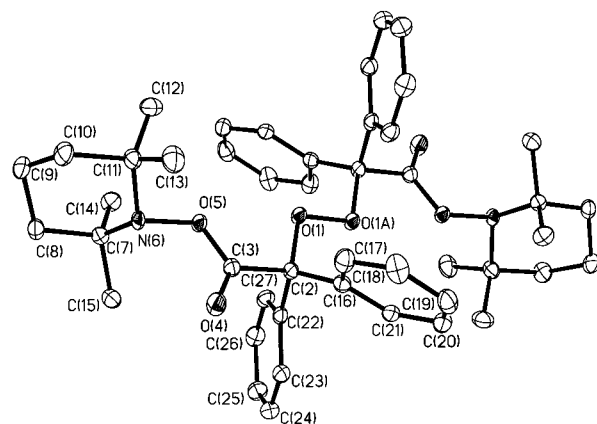
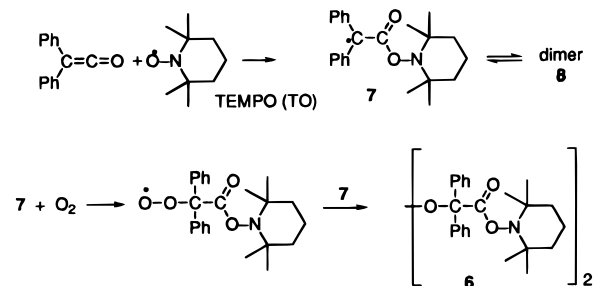


Figure 1. X-ray structure of peroxide **6**.

Scheme 1



separated from excess TEMPO by chromatography. Upon allowing the mixture to stand in air, a crystalline solid separated out (18% yield, mp 150–152 °C, dec.) that was identified by its spectral properties as the peroxide **6**, and this assignment was confirmed by an X-ray crystal structure (Figure 1).^{5b} The structure of **6** is characterized by a 180.0° $\text{C}-\text{O}-\text{O}-\text{C}$ dihedral angle, as also found in $\text{Ph}_3\text{COOCPh}_3$.^{6a} This geometry is uncommon for peroxides and is presumably due to steric effects. The properties of related peroxides have been of interest,^{6b–k} including $(\text{OCPh}_2\text{CO}_2\text{Et})_2$, mp 116–118 °C (dec.),^{6g} and the corresponding methyl ester, mp 151–152 °C.^{6h}

A plausible route to **6** beginning with attack of TEMPO on C_α of the ketene is shown in Scheme 1. The presumed dimer **8** was not characterized but, based on information from other carboxydiarylmethyl radicals, would evidently be a head-to-tail dimer.⁷

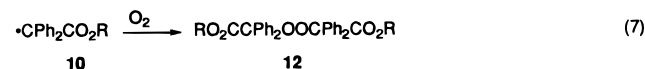
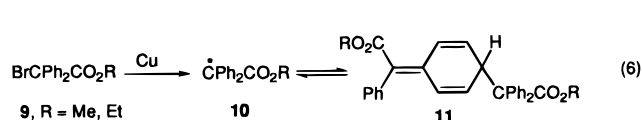
Analogy for this reaction pathway forming **6** is found in the conversion of the halo esters **9** to radicals **10**, which were in

(5) (a) Gaussian 94, Revision D.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995. (b) Details are given in the Supporting Information.

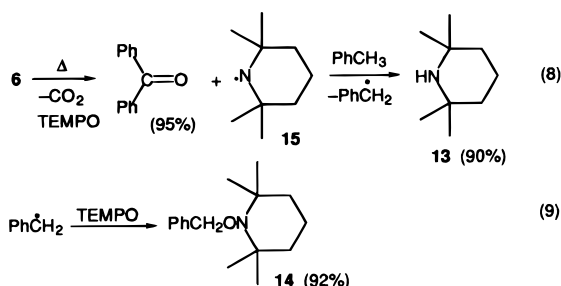
(7) (a) Kubiak, B.; Lehnig, M.; Neumann, W. P.; Pentling, U.; Zarkadis, A. K. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1443–1447. (b) Neumann, W. P.; Stapel, R. *Chem. Ber.* **1986**, *119*, 3422–3431.

(8) (a) Carloni, P.; Damiani, E.; Iacussi, M.; Greci, L.; Stipa, P.; Cauzi, D.; Rizzoli, C.; Sgarabotto, P. *Tetrahedron* **1995**, *51*, 12445–12452. (b) Lucarini, M.; Marchesi, E.; Pedulli, G. F.; Chatgililoglu, C. *J. Org. Chem.* **1998**, *63*, 1687–1693. (c) Roberts, J. R.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 3228–3235.

equilibrium with the head-to-tail dimers **11**.⁷ Reaction of the radicals **10** with O₂ formed the peroxides **12**,^{6g,h} but the reactivity of these peroxides has not been examined.



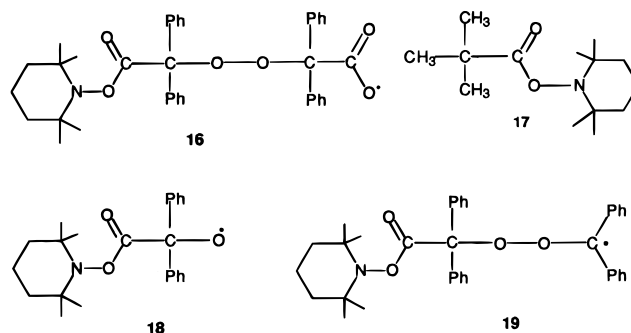
Heating **6** for 8 h in toluene in the presence of 4 equiv of TEMPO at 100 °C gave benzophenone (95%), tetramethylpiperidine (**13**, 90%), and **14** (92%). These products indicate that **6** undergoes thermal cleavage to form Ph₂C=O, CO₂, and tetramethylpiperidiny radicals **15**,⁸ which abstract hydrogen from toluene (eqs 8 and 9).



The kinetics of the decomposition of **6** in *n*-octane were monitored by observation of the increase in the Ph₂C=O absorption maximum at 245 nm ($k_{\text{obs}} = 3.59 \times 10^{-5} \text{ s}^{-1}$ at 85.0 °C, $\Delta H^\ddagger = 34.3 \pm 0.3 \text{ kcal/mol}$, $\Delta S^\ddagger = 16.7 \pm 0.7 \text{ cal K}^{-1} \text{ mol}^{-1}$).^{5b} Decomposition kinetics have not been measured for (Ph₃CO)₂, which is reported to decompose in 8 min in boiling xylene (bp of *p*-xylene: 135 °C) with O–O bond cleavage,^{6b} but for dicumyl peroxide, (PhMe₂CO)₂, a rate constant k of $1.5 \times 10^{-4} \text{ s}^{-1}$ at 135 °C may be calculated, or a half-life of 1.3 h.^{6c} The extrapolated rate constant for **6** at 135 °C is $1.5 \times 10^{-2} \text{ s}^{-1}$, or 100 times greater than for (PhMe₂CO)₂. The radicals Ph₃CO•^{6b} and Ph₂C(CH₃)O• (from [Ph₂C(CH₃)OO-*t*-Bu]^{6d}) undergo facile 1,2-phenyl migration from C to O (Wieland rearrangement) to form the radicals Ph₂C•OPh and PhC•(CH₃)OPh, respectively. The rate constant of the rearrangement of Ph₃CO• has been reported^{6e} to exceed $5 \times 10^{10} \text{ s}^{-1}$. The radical Ph₂C(CH₃)O• does not lose CH₃• to form benzophenone but undergoes phenyl migration with a lifetime of $3 \times 10^{-7} \text{ s}$.

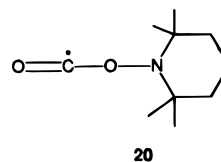
The higher reactivity of **6** compared to (PhMe₂CO)₂ is presumably not due to rate-limiting N–O bond fission of **6** to form the transient radical **16** because the acyloxypiperidine derivative **17**^a is stable at 150 °C, and **6** and **17** should have comparable reactivity by this pathway. Other possible causes of the observed rate enhancement are steric acceleration and rate-enhancing synchronous bond cleavage in **6**. In the X-ray structure of **6** (Figure 1), significant steric crowding is apparent that could be relieved upon cleavage of the O–O bond with formation of **18**. Steric effects in dialkyl peroxide decompositions have been demonstrated by Hendrickson et al.,^{6k} for example for (*t*-BuCMe₂O)₂, which is less reactive than **6** at 125 °C by a factor of only 10.8. The cleavage of **18**, forming Ph₂C=

O, would have to be rapid to exceed the rate of phenyl migration to oxygen in the radical Ph₂C(CH₃)O• noted above.



Possible multiple bond scission may also be considered, and in the case of the thermolysis of *tert*-butyl peresters RCO₃-*t*-Bu, it was proposed by Bartlett and Hiatt^{9b} that the activation parameters of these reactions could be used as a criterion of the reaction mechanism, in that in cases where multiple bond breaking in the transition state occurred there would be a freezing out in the transition state of rotational motions that were free in the reactants, and this would be reflected in lowered entropies of activation. Pryor and Smith^{9c} examined the application of this analysis to dialkyl and diacyl peroxides and concluded that this correlation could be used "in limited and rather imprecise ways". The activation parameter data for **6** fall between the regions laid out by Pryor and Smith^{9c} for rate-limiting one and two bond scissions, and so either pathway is possible by this criterion.

In the thermolysis of **6** a total of five bonds are cleaved, and plausible pathways involving synchronous cleavage of two bonds would be breaking of N–O and C–C bonds, giving **19**, or cleavage of O–O and C–C bonds, giving **18** and **20**.



Cleavage of even more bonds in the rate-limiting step would be well outside the expectations of the analysis of Pryor and Smith.^{9c} Since steric effects alone with rate-limiting cleavage of the O–O bond appear sufficient to account for the rate and activation parameter data this mechanism appears most reasonable, with subsequent rapid cleavage of further bonds to give the observed products.

To test the generality of the conversion of diarylketenes to peroxides, the previously unreported ketene (4-ClC₆H₄)₂C=C=O (**21**) was prepared by dehydrochlorination of the acyl chloride and was identified by its characteristic IR signal at 2103 cm⁻¹ and other spectral data. This ketene was reacted without purification with TEMPO and was rapidly consumed as

(9) (a) Anderson, J. E.; Corrie, J. E. T. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1027–1031. (b) Bartlett, P. D.; Hiatt, R. R. *J. Am. Chem. Soc.* **1958**, *80*, 1398–1408. (c) Pryor, W. A.; Smith, K. *Int. J. Chem. Kinet.* **1971**, *3*, 387–394.

(10) (a) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *Acc. Chem. Res.* **1995**, *28*, 265–271. (b) Zhao, D.-c.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993**, *115*, 10097–10103. (c) Brown, R. S.; Christl, M.; Lough, A. J.; Ma, J.; Peters, E.-M.; Peters, K.; Sammler, F.; Sung, K.; Slesbocka-Tilk, H.; Tidwell, T. T. *J. Org. Chem.* **1998**, *63*, 6000–6006. (d) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *J. Chem. Soc., Perkin Trans. 2* **1995**, 847–851. (e) Colomvakos, J. D.; Egle, I.; Egle, I.; Ma, J.; Pole, D. L.; Tidwell, T. T.; Warkentin, J. J. *Org. Chem.* **1996**, *61*, 9522–9527. (f) Adam, W.; Bottle, S. E.; Grice, I. D.; Pfeiler, D.; Wentrup, C. *Tetrahedron Lett.* **1996**, *37*, 2113–2116. (g) Huang, W.; Fang, D.; Temple, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 2832–2838.

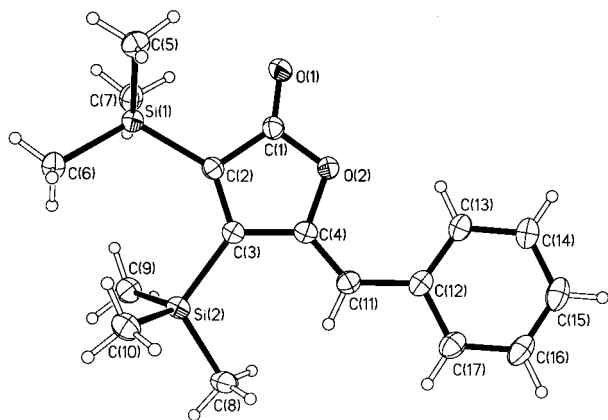
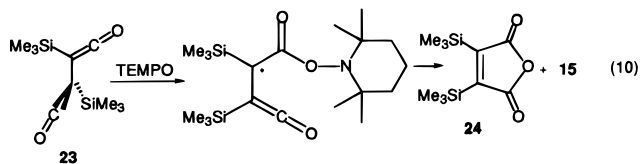


Figure 2. X-ray structure of lactone **27**.

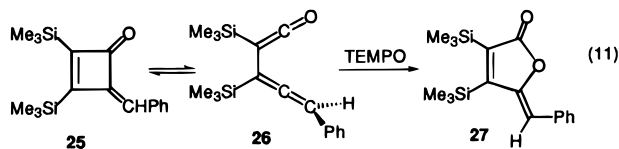
indicated by the color change. The resulting intermediate was reacted with a stream of oxygen to give the peroxide $[\text{TO}_2\text{-CCAr}_2\text{O}]_2$ (**22**, Ar = 4-ClC₆H₄) in 44% yield. In this case the intermediate radical $\cdot\text{CAR}_2\text{CO}_2\text{T}$ may form a head-to-head dimer.^{7b}

The reactivity of TEMPO with the 1,2-bisketene ($\text{Me}_3\text{SiC}=\text{C}=\text{O}$) (**23**)^{10a} was also examined. Bisketene **23** reacts readily with many reagents, including H₂O,^{10b} Br₂,^{10c} protic acids,^{10d} and cycloaddition reagents,^{10e} and with H₂O is 10⁴ less reactive than Ph₂C=C=O. With TEMPO in toluene at 90 °C, **23** forms in 3 h the maleic anhydride **24**^{10b} (80%), **13** (85%), and **14** (76%). A possible mechanism for the formation of **24** is shown (eq 10) and resembles that suggested^{10b} for the formation of **24**



by the reaction of **23** with O₂, although the latter process occurred in low yield. The related reaction of the radical species NO with bisketenes was examined and proposed^{10f} to involve N–C bond formation, which is unlikely for TEMPO.

This oxygenation procedure is also found to occur for an analogous allenylketene, providing a route to a butenolide derivative. Methylenecyclobutenone **25** and allenylketene **26** are both present at thermal equilibrium, but upon photolysis, complete conversion to **26** occurs.^{10g} Heating **26** made in this way in toluene with TEMPO at 180 °C for 3 h gave the lactone **27** in 61% yield (eq 11), with concomitant formation of 50%



13 and 55% **14**. The stereochemistry of **27** was established by X-ray crystallography (Figure 2). This process presumably occurs by a mechanism resembling that of eq 10 and involves rotation of the phenyl group away from the nearby Me₃Si group. The details of this process are the subject of further investigation.

In summary, the reaction of TEMPO with diaryl ketenes has been shown to be a facile process that provides a simple preparation of novel peroxidic free radical initiators and of

aminyl radicals.¹¹ The properties of novel difunctional initiators have been of continuing interest,¹² and examples containing TEMPO and diazene moieties have been reported for the preparation of block polymers.^{12a} The reactions of TEMPO with 1,2-bisketene **23** and allenylketene **26** occur with oxygenation and also give aminyl radicals. The extension of this reaction to other ketene types is underway and promises to reveal further novel chemistry.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer FTIR 1000 spectrometer. ¹H NMR spectra were recorded on a Varian VXR-200 instrument at 199.975 MHz or a Varian Unity-400 instrument at 399.443 MHz referenced to residual CHCl₃ (7.26 ppm). ¹³C NMR spectra were recorded at 100.577 MHz and referenced to the center line of CDCl₃ (77.00 ppm). GC analyses were performed on a Perkin-Elmer Auto-system XL gas chromatograph using a Simplicity 5 column and FID detector.

Reaction between Diphenylketene and TEMPO. To a solution of diphenylketene (0.11 g, 0.57 mmol)¹³ in 3 mL of CDCl₃ was added TEMPO (0.18 g, 1.15 mmol). The reaction mixture was stirred 2 h at 25 °C, the solvent was evaporated, and the residue was chromatographed over silica gel (5% EtOAc/hexanes). The elutant, on standing in air for 3 day, gave peroxide **6** (37 mg, 18%) as a white crystalline solid: mp 150–152 °C; IR (CDCl₃) 1764 cm⁻¹; ¹H NMR (CDCl₃) δ 0.744 (s, 12, CH₃), 1.025 (s, 12, CH₃), 1.34–1.62 (m, 12, CH₂), 7.14–7.28 (m, 20, Ph); ¹³C NMR (CDCl₃) δ 16.87, 20.75, 31.37, 39.51, 60.53, 92.26, 127.30, 127.72, 129.73, 138.57, 169.39.

Bis(4-chlorophenyl)ketene (21). To bis(4-chlorophenyl)acetyl chloride (1.0 g, 3.3 mmol) in 25 mL of ethyl ether was added Et₃N (0.5 mL, 3.6 mmol) dropwise at 0 °C, and the reaction mixture was stirred 4 h at 0 °C.¹³ The Et₃NHCl was filtered off and washed with ether, the solvent was evaporated, and the crude ketene **21** was used without further purification: IR (CDCl₃) 2103 cm⁻¹; ¹H NMR (CDCl₃) δ 7.10–7.14 (m, 4, Ar), 7.32–7.36 (m, 4, Ar); ¹³C NMR (CDCl₃) δ 45.83, 128.76, 129.51, 131.32, 132.06, 199.61.

Reaction between 21 and TEMPO. To **21** (0.35 g, 1.3 mmol) in 20 mL of dichloromethane was added TEMPO (0.24 g, 1.5 mmol) in one portion at 0 °C. The ice bath was removed, and the mixture was stirred for 0.5 h. Then oxygen was bubbled through the reaction mixture for 2 h. After evaporation of the solvent, the residue was dissolved in 50 mL of methanol and H₂O was added to precipitate the peroxide, giving 254 mg (44%) of peroxide **22** as a light yellow solid. The crude product was purified by flash chromatography using 3% EtOAc in hexanes and recrystallized from pentane to give pure peroxide: mp 147–149 °C; IR (CDCl₃) 1762 cm⁻¹; ¹H NMR (CDCl₃) δ 0.77 (s, 12, CH₃), 1.02 (s, 12, CH₃), 1.3–1.7 (m, 12, CH₂), 7.16 (s, 16, Ar); ¹³C NMR (CDCl₃) δ 16.77, 20.76, 31.42, 39.41, 60.71, 91.16, 127.71, 130.71, 134.38, 136.21, 168.54.

Decomposition of Peroxide 6. A mixture of peroxide **6** (10.6 mg, 0.014 mmol) and TEMPO (9.2 mg, 0.059 mmol) in 1 mL of toluene was heated in an oil bath at 100 °C 8 h under nitrogen. The solvent and volatile products were removed in vacuo and collected in a trap cooled by liquid N₂. GC analysis using aniline as an internal standard showed the presence of 3.7 mg of **13** (90%). The residue of the reaction mixture was dissolved in 5 mL of diethyl ether and washed twice with 5 mL of 10% HCl. The ether layer was dried over anhydrous MgSO₄. Flash chromatography gave benzophenone (4.9 mg, 95%) as a gum: ¹H NMR δ 7.4–7.9 (m); IR (CH₂Cl₂) 1659 cm⁻¹. The aqueous layer

(12) (a) Gravert, D. J.; Datta, A.; Wentworth, P., Jr.; Janda, K. D. *J. Am. Chem. Soc.* **1998**, *120*, 9481–9495. (b) Engel, P. S.; He, S. L.; Smith, W. B. *J. Am. Chem. Soc.* **1997**, *119*, 6059–6065. (c) Engel, P. S.; Wu, A. *J. Org. Chem.* **1994**, *59*, 3969–3974. (d) Engel, P. S.; Wang, C.; Chen, Y.; Rüdhardt, C.; Beckhaus, H.-D. *J. Am. Chem. Soc.* **1993**, *115*, 65–74. (e) Lai, L.-F.; Tidwell, T. T. *J. Am. Chem. Soc.* **1977**, *99*, 1465–1470.

(13) Taylor, E. C.; McKillop, A.; Hawks, G. H. *Organic Synthesis*; Noland, W. E., Ed.; Wiley: New York, 1988; Collect. Vol 6, pp 549–551.

(14) (a) Korolenko, E. C.; Cozens, F. L.; Scaiano, J. C. *J. Phys. Chem.* **1995**, *99*, 14123–14128. (b) Brown, T. M.; Cooksey, C. J.; Crich, D.; Dronsfield, A. T.; Ellis, R.; *J. Chem. Soc., Perkin Trans. 1* **1993**, 2131–2136.

(11) Musa, O. M.; Horner, J. H.; Shahin, H.; Newcombe, M. *J. Am. Chem. Soc.* **1996**, *118*, 3862–3868.

was neutralized by NaHCO₃ and extracted by diethyl ether (3 × 10 mL). The ether extract was dried over anhydrous MgSO₄. Flash chromatography gave **14**¹⁴ (6.6 mg, 92%).

Kinetic Study of Decomposition of Peroxide 6. The kinetics of the decomposition of peroxide **6** were measured over the range 75.7–99.1 °C in octane by monitoring the increase in the absorption of benzophenone at 245.3 nm, where the largest change occurred. The measured rate constants are given in Table 1 (Supporting Information).

Reaction between Bisketene 23 and TEMPO in CDCl₃. A mixture of bisketene **23** (0.151 g, 0.67 mmol) and TEMPO (0.209 g, 1.34 mmol) in 1 mL of CDCl₃ in a vial under nitrogen was heated 3 h at 100 °C. After evaporation of the solvent, the crude product was purified by chromatography (5% EtOAc/hexanes), giving anhydride **24**^{10b} (69.8 mg, 43%) as a gum: IR (CDCl₃) 1812 (w), 1748, (s) cm⁻¹; ¹H NMR (CDCl₃) δ 0.387; ¹³C NMR (CDCl₃) δ 0.02, 164.40, 168.31.

Reaction between Bisketene 23 and TEMPO in Toluene. A mixture of bisketene **23** (0.143 g, 0.631 mmol) and TEMPO (0.295 g, 1.89 mmol) in 1 mL of toluene was heated in an oil bath at 90 °C for 3 h under nitrogen. The volatile components of the reaction mixture were removed by a vacuum pump at room temperature and were collected in a trap cooled with liquid nitrogen. GC analysis using aniline as an internal standard showed that the volatile part of the reaction mixture contained 0.075 g (85%) of **13**. The residue of the reaction mixture (nonvolatile) was dissolved in 10 mL of diethyl ether and washed twice with 10 mL of 10% HCl aqueous solution. The ether layer was dried over anhydrous MgSO₄. Flash chromatography gave anhydride **24** (0.122 g, 80%) as a gum. The aqueous layer was neutralized by NaHCO₃ and then extracted by diethyl ether (3 × 20 mL). The ether extract was dried over anhydrous MgSO₄. Flash chromatography gave **14**¹⁴ (0.119 g, 76%) as a liquid: ¹H NMR (CDCl₃) δ 1.16 (s, 6), 1.27 (s, 6), 1.3–1.8 (m, 6), 4.84 (s, 2), 7.3–7.4 (m, 5); ¹³C NMR (CDCl₃) δ 17.11, 20.29, 33.07, 39.71, 60.00, 78.71, 127.26, 127.43, 128.20, 138.10.

Reaction between Allenylketene 26 and TEMPO in Toluene. A mixture of allenylketene **26** (0.0795 g, 0.265 mmol), formed by photolysis of **25**,^{10e} and TEMPO (0.1242 g, 0.796 mmol) in 1 mL of toluene was sealed in a vial under nitrogen and was heated 3 h in an oil bath at 180 °C. The volatile components of the reaction mixture were analyzed as above to contain 0.019 g (50%) of **13**. The nonvolatile residue was dissolved in 10 mL of diethyl ether and washed twice with 10 mL of 10% HCl aqueous solution. The ether layer was dried over anhydrous MgSO₄. Flash chromatography gave lactone **27** (50.9 mg, 61%) as a white solid: mp 82–83 °C; IR (CDCl₃) 1737 cm⁻¹ (C=O); ¹H NMR (CDCl₃) δ 0.377 (s, 9, TMS), 0.466 (s, 9, TMS), 6.21 (s, 1, =CH), 7.30–7.81 (m, 5, Ph); ¹³C NMR (CDCl₃) δ 0.689, 1.929, 113.34, 128.68, 128.73, 130.68, 133.81, 140.25, 153.32, 167.57, 173.40; EIMS *m/z* 316 (M⁺, 17), 157 (19), 142 (100), 118 (36), 73 (Me₃Si⁺, 18); HRMS calcd for C₁₇H₂₄O₂Si₂ 316.1315, found 316.1314. Lactone **27** was recrystallized from pentane and a crystal was submitted for X-ray analysis. The aqueous layer was neutralized by NaHCO₃ and then extracted by diethyl ether (3 × 20 mL). The ether extract was dried over anhydrous MgSO₄. Flash chromatography gave **14** (36.2 mg, 55%).

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. This paper is dedicated to Dr. Keith U. Ingold on the occasion of his 70th birthday, in recognition of his many contributions to the study of free radicals.

Supporting Information Available: Computational data and NMR spectra, kinetic data, X-ray structural information on **6** and **27** (PDF) and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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