Nitroxyl Radical Reactions with 4-Pentenyl- and Cyclopropylketenes: New Routes to 5-Hexenyl- and Cyclopropylmethyl Radicals

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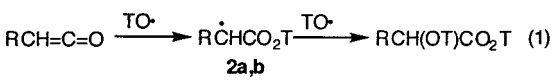
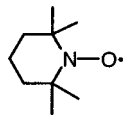
4-Pentenylketenes **4a** and **9** and cyclopropylketenes **3a**, **13**, **14** (RCH═C═O) are generated by photochemical Wolff rearrangements and observed by IR as relatively long-lived species at room temperature in hydrocarbon solvents. The reactions of these ketenes with the nitroxyl radicals tetramethylpiperidinyloxyl (TEMPO, TO•) and tetramethylisoindoline-2-oxyl (TMIO, IO•) form carboxy substituted 5-hexenyl and cyclopropylmethyl radicals which are either trapped by a second nitroxyl radical or undergo rearrangements followed by trapping. The rate constant of the reaction of **4a** with TEMPO was similar to that of *n*-BuCH═C═O (**1b**), while **3a** was 4.3 times more reactive, indicating cyclopropyl stabilization of the incipient radical.

Recent theoretical[1a,b] and experimental[1b−f] studies in our laboratory have shown that ketenes **1** react with the aminoxyl radical tetramethylpiperidinyloxyl (TEMPO, TO•) by initial attack at the ketenyl carbon forming α-acyl radicals **2**, which then typically react with a second TEMPO molecule (eq 1), sometimes with rearrangement. This pathway is in accord with the prediction of molecular orbital calculations,[1a,b,g,h] and is supported by the effect of the substituents R on the reactivity, including a qualitative correlation (eq 2) of the rate constants for reaction with TEMPO with the corresponding rate constants for hydration of the same ketenes in H_2O.[1c,d]



1a (R = Ph), **1b** (R = n-Bu)



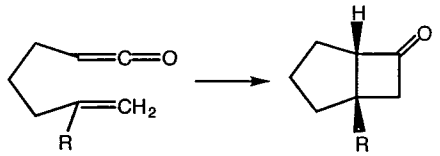
TEMPO, TO•

$$\log k_2(\text{TEMPO}) = 1.14 \log k(H_2O) - 3.71 \qquad (2)$$

This reaction provides a new method for forming radicals **2** with functional groups in the side chain R that may interact with the carbon centered radical generated in **2**.[2] The current study involves ketenes **1** where R is a 4-pentenyl group which may undergo cyclization[3] or a cyclopropyl group which may undergo ring opening.[4] Both of these reactions are of widespread utility in free radical chemistry. In previous investigations we have studied the preparation and reactivity of cyclopropylketenes **3**,[5] while 4-pentenylketenes have been found to undergo thermal intramolecular cycloadditions in some cases (eq 3).[6] There

c–PrCR=C=O

R = H (**3a**), Ph (**3b**), c–Pr (**3c**), t–Bu (**3d**)



(3)

4a (R = H), **4b** (R = Me) (3%, R = H; 80% R = Me)

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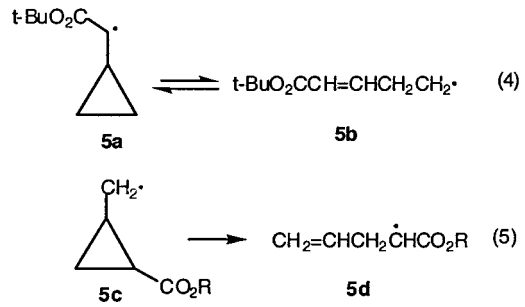
have however been no previous studies of free radical reactions of such ketenes.

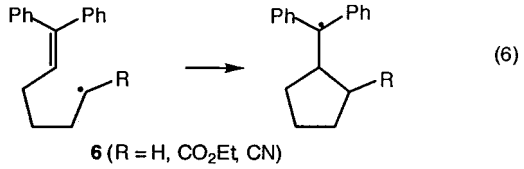
The trapping reactions of radicals by nitroxyls such as TEMPO have widespread application[7,8] and other nitroxyl radicals have also been used for this purpose, for example 1,1,3,3-tetramethylisoindoline-2-yloxyl (TMIO)[9] and $(CF_3)_2NO\bullet$.[10] The relative reactivities of TMIO compared to TEMPO range from 1.04 to 1.9[9b] toward a number of radicals, with the greater selectivities for less reactive radicals. The radical TMIO• has the advantages relative to TEMPO that it is usually more readily separated from reaction products by chromatography, and the addition products from this radical also possess a UV chromophore that aids in spectral analysis. A disadvantage is that this radical is not commercially available. The radical $(CF_3)_2NO\bullet$ forms a 1,2-diadduct with $Ph_2C{=}C{=}O$,[10d] but is less convenient to prepare, and is also highly volatile so that more care is needed in handling.

As shown in eq 1 addition of TEMPO to a ketene forms a radical adjacent to an acyloxy group, and such radicals formed by abstraction reactions[3c−g] or by oxidation of enolates[7c] have been applied in synthesis. α-Acyl groups stabilize carbon-centered radicals.[4c,11] Thus the formation of carbon centered radicals substituted with α-CO_2R or α-CN groups by radical additions to acrylate esters and acrylonitrile,[12a,b] cyclization of 6-cyano-5-hexenyl radicals[3a,b] and cyclization of radical **5b** (eq 4),[12c] and by ring opening of 2-carboalkoxyl substituted cyclopropyl radicals **5c** (eq 5)[12d,e] are strongly accelerated by factors of 10^3 relative

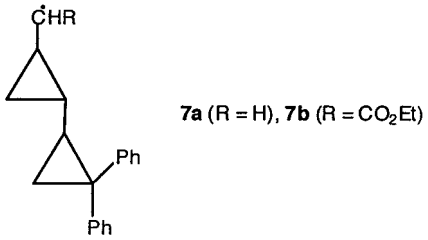


to formation of the corresponding radicals substituted by H or alkyl. Reaction of TMIO with $CH_2{=}CHCN$ and with $CH_2{=}CHCO_2Et$ also occurs at 110 °C forming the products of 1,2-addition of two TMIO radicals.[12g]

Beckwith and Bowry[4b] estimated a rate ratio of $k_H/k_{CO_2Bu-t} = 20-50$ for ring opening in cyclohexane of the parent cyclopropylmethyl radical relative to **5a** (eq 4). However, cyclization of 6,6-diphenylhexenyl radicals **6** showed no change in the rate constant for CO_2Et or CN relative to H (eq 6).[11]



Later studies by Horner, Tanaka, and Newcomb[4c] showed that in THF solvent at 20 °C that for **7** the rate ratio k_H/k_{CO_2Et} was only 1.1. However while the solvent effect on the ring opening of **7a** was negligible the rate ratio k_{CH_3CN}/k_{THF} for **7b** was 1.8 at 20 °C, and this acceleration in the reaction of the ester substituted substrate in the more polar solvent suggests that in hydrocarbon solvents a larger k_H/k_{CO_2R} rate ratio might be anticipated. The conjugative stabilization of the acrylate esters formed by ring opening of **5a** and **7b** is cited as one cause of the facility of this process.[4c]



Results

Because of the significant influence of carboalkoxy substituents on radical rearrangements as outlined above and because of our discovery[1a−f] of the generality of aminoxyl addition to ketenes we have undertaken a systematic study of the reactions of aminoxyl radicals with ketenes bearing cyclopropyl and alkenyl side chains and the examination of the reactions of the substituted α-acyl radicals formed. 1-Diazo-6-hepten-2-one (**8a**)[13a,b] was prepared by reaction of the acyl chloride with diazomethane as has been described.[13] 1-Diazo-7-phenyl-6-hepten-2-one (**8b**)[13b] was prepared similarly from the acyl chloride of the acid obtained by the reaction of the

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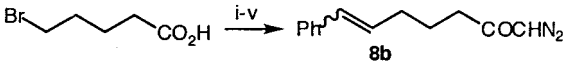
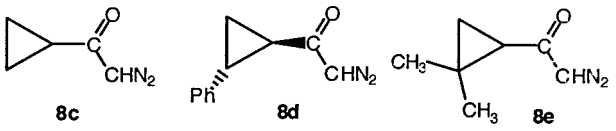
Wittig reagent[13c] derived from 5-bromovaleric acid with benzaldehyde as an 87/13 *E*/*Z* mixture (eq 7). The cyclopropyl diazo ketones **8c**−**e** were also prepared from the corresponding acyl chlorides by reaction with diazomethane.

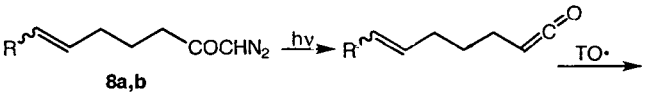


(7)

i) Ph_3P, ii) $(Me_3Si)_2NLi$, iii) PhCHO , iv) $(COCl)_2$, v) CH_2N_2



Photolysis of the 5-pentenyl and 6-phenyl-5-pentenyl diazo ketones (**8a,b**, respectively) in pentane with 250 nm light gave the ketenes **4a** and **9** as identified by their IR bands at 2120.5 and 2119.5 cm^{-1}, respectively. Addition of 2.1 equivalents of TEMPO to the preformed ketenes **4a** and **9** to form the radicals **10a,b** gave the 1,2-diaddition products (**11a,b**) in 63 and 67% yields, respectively, after chromatography (eq 8). Cyclobutanone products from ketene cyclization or cyclopentane products from radical cyclization were not detected.



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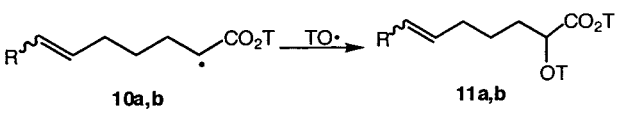
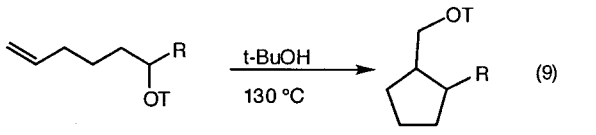


Cyclization of **11a** was achieved using the method of Studer,[3f] who found heating of the 5-hexenyl-1-phenyl substituted TEMPO substituted adduct **11c** gave eventual cyclization to **12b** of the reversibly formed 5-hexenyl radical. For **11a** this gave the cyclized product **12a** (74%) as a *cis*/*trans* mixture (eq 9). However, this procedure lacks generality as comparable treatment of **11b** did not give a cyclized product, but instead gave more complex reactions. The thermal reactivities of **11b** and other bis(TEMPO) adducts of ketenes are under investigation.



(9)

Cyclopropylketene (**3a**), *trans*-2-phenylcyclopropylketene (**13**), and 2,2-dimethylcyclopropylketene (**14**) were generated by photolysis of the corresponding diazo ketones, and identified by their IR bands at 2120, 2121, and 2119 cm^{-1}, respectively. Addition of TEMPO to **3a** at 25 °C gave the ring closed and ring opened adducts **17a** and **18a** in a 1/1.6 ratio (Scheme). Upon chromatography **17a** (7%) and E/Z-**18a** (11%) were isolated. Reaction of **13** gave only ring opened adducts, which upon chromatography gave the elimination product 2-*Z*,4-*E*−**21**, *Z*-**20a** (14%), and a mixture of *E*−**20a** and *E*,*E*−**21** (55%). Similarly **14** gave **24a** (Z, 6%; *E*, 18%) after chromatography. The substituents in **20a** and **23** evidently promote elimination.

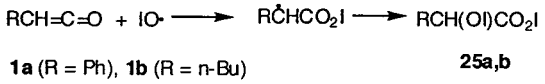
Table 1. Rate Constants for Ketene Reactions with Aminoxyl Radicals in Isooctane at 25 °C

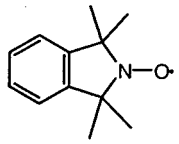
ketene	radical	k_2 (M^{-1} s^{-1})	k_{rel}
PhCH=C=O **(1a)**	IO•	6.99×10^{-1}	1.0×10^3
	TO•	1.26[a]	1.0×10^3
n-BuCH=C=O **(1b)**	IO•	6.95×10^{-4}	1.0
	TO•	1.22×10^{-3}[b]	1.0
c-PrCH=C=O **(3a)**	TO•	5.26×10^{-3}	4.3
CH_2=CH(CH_2)$_3$CH=C=O (**4a**)	TO•	1.89×10^{-3}	1.6

[a] Ref 1c. [b] Ref 1d.

Rates for the reaction of **3a** and **4a** with excess TEMPO in isooctane were measured by observing the decrease in the ketene absorption by UV spectroscopy as we have reported previously,[1c,d] and the derived rate constants are reported in Table 1.

Because of the utility of the tetramethylisoindoline-2-oxyl radical (TMIO, IO•) the reactions of this radical with ketenes were also studied. Phenylketene (**1a**) and *n*-butylketene (**1b**) were generated in pentane by photolysis of the corresponding diazo ketones and addition of IO• resulted in the isolation of the 1,2-bis(addition) products **25a,b**, in 30 and 38% yield, respectively. Based on previous studies using TEMPO these reactions proceed by initial attack at the carbonyl carbon of the ketene (eq 10). The kinetics of these reactions in isooctane were measured by observing the decrease of the ketene absorption by UV in the presence of excess TMIO, and the derived rate constants are given in Table 1.





TMIO, IO•

(10)

The reactions of TMIO with cyclopropylketene (**3a**) at 25 °C with analysis of the initial product mixture by ^1H NMR showed the ring closed and ring opened products **17b** and **18b** were formed in a 2/1 ratio, whereas reaction at 50 °C gave a product ratio of 1/2. Separation of the product from reaction at 50 °C gave the ring closed and ring opened products **17b** (29%) and *E*−**18b** (8%). The inefficient isolation of *E*−**18b** is due to difficulties with the chromatographic separation. Reaction of TMIO with **13** at 25 °C gave after chromatography the ring opened *Z*-**20b** (14%) and *E*−**20b** (25%), without diene product from elimination. Reaction of **14** with TMIO at 25 °C gave after chromatography the elimination products *Z*-**24b** (7%) and *E*−**24b** (53%). The identification of the products followed from their spectral properties, including COSY, HSQC, TOCSY, and HMBC NMR studies of **20**.

Discussion

The rate constants for ring opening of the cyclopropylmethyl radical[4c] and ring closure of the 5-hexenyl radical are reported as 4.0×10^8 s^{-1} at 20 °C, essentially independent of solvent, and 2.3×10^5 s^{-1}, respectively.

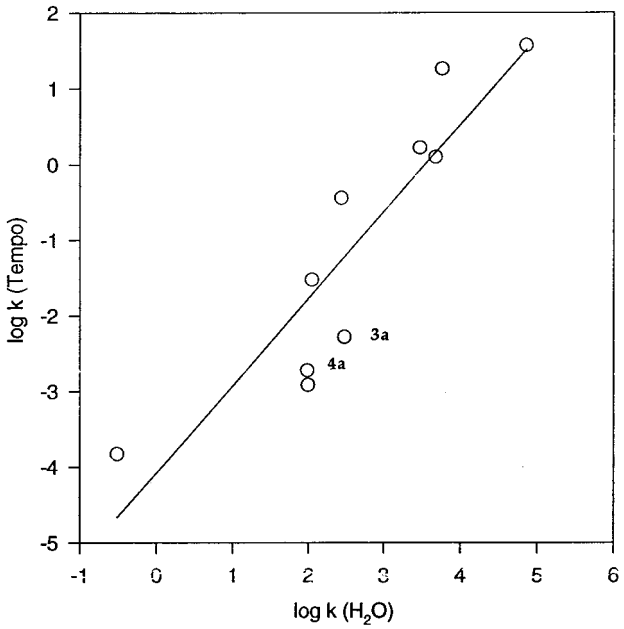


Figure 1. Plot of log k_2(TEMPO) vs log k_{H_2O} for ketenes with points for **3a** and **4a**.

The ratio of ring closed to ring opened products of the cyclopropylmethyl radicals **15** was 1/1.6 for capture by TEMPO at 25 °C but 2/1 for TMIO, suggesting that TMIO is more efficient at capturing the initial radical than is TEMPO. For the 2-phenylcyclopropylmethyl radicals **19** only ring opening was observed in both cases, consistent with the acceleration of ring opening by the phenyl on the cyclopropyl ring.

The rate constants for the addition of TEMPO to phenylketene (**1a**) and *n*-butylketene (**1b**) exceed those for the corresponding reactions of TMIO by a factor of 1.8 in both cases (Table 1). This differs from the greater reactivity of TMIO compared to TEMPO in reactions with radicals noted above, and by others.[9b] A possible explanation of this reversal is that the reaction with ketenes has a later transition state and the more rigid TMIO suffers from steric crowding.

The relative rate constants for the reaction of ketenes RCH=C=O with TEMPO for R = Ph,[1c] *c*-Pr, CH_2=$CHCH_2$-CH_2, and *n*-Bu are 1.0×10^3, 4.3, 1.6, and 1.0, respectively. The strong acceleration by Ph is expected because of the conjugative ability of this group in stabilizing the resultant radical. Cyclopropyl groups are known to stabilize free radicals,[14] and the effect of the *c*-Pr group on the addition of TEMPO to ketene demonstrates a small but significant accelerating effect. The 4-pentenyl and *n*-butyl substituted ketenes have similar reactivities, as expected.

The rate constant for hydration of *c*-PrCH=C=O (**3a**) has been reported previously,[5c] and on the assumption that the rate constant for hydration of 4-pentenylketene (**4a**) is similar to that of *n*-butyl ketene (**1b**) then the reactivities of both **3a** and **4a** can be fit to the previous correlation of TEMPO and H_2O reactivities with ketenes (eq 2),[1c,d] as shown in Figure 1. The reasonable fit of these values to the plot lends confidence in the predictive value of this correlation.

The capture of the 4-pentenylketene **4a** by TEMPO to give the uncyclized adduct **11a** of addition of two TEMPO molecules (eq 8) demonstrates that capture of the radical **10a** is faster than cyclization. However **11a** was isomerized to the cyclized adduct **12a** (eq 9), showing that **10a** is formed reversibly and can undergo cyclization to form **12a**. However the failure of the 5-phenyl adduct **11b** to give a cyclized product is indicative of a more complicated reaction pathway, and this is currently under investigation.

For the cyclopropylketene **3a** the competitive formation of ring-closed adducts **17** and ring opened adducts **18** indicates the rate of capture of the initial radicals **15** and the rate of irreversible ring opening (Scheme 1) are finely balanced. As noted above the reaction of **3a** with TMIO gave a higher proportion of ring closed product, showing that TMIO was moderately more reactive toward the intermediate acyl radical than is TEMPO. This agrees with the absolute rate data noted above.[9b]

The presence of radical stabilizing groups on the cyclopropyl rings in **13** and **14** changes the reaction to complete ring opening in both cases. This is expected because of the significant acceleration of cyclopropyl ring opening which has been found for phenyl and methyl groups.

In summary the reactions of aminoxyl radicals with 4-pentenyl- and cyclopropylketenes have been demonstrated and provide a new route to carboxy substituted 4-pentenyl and cyclopropylmethyl radicals which undergo the characteristic ring closing and ring opening reactions, respectively, of these substrates. The kinetics of the reactions of *n*-butyl, 4-pentenyl-, and cyclopropylketenes with aminoxyl radicals have been measured and the rate constants confirm that the reactions proceed with initial radical attack on the carbonyl carbon, with a moderate rate enhancing effect of cyclopropyl due to its stabilization of the α-acyl radical.

Experimental Section

Glassware was oven-dried (140 °C) overnight while all plastic equipment and microliter syringes were kept in a desiccator. All ketene reactions were carried out in solutions degassed with argon or nitrogen. Ether and toluene were distilled from Na/benzophenone just prior to use. Dichloromethane, pentane and 2,2,4-trimethylpentane were all stored over 4 Å molecular sieves. Deuterated chloroform was kept over potassium carbonate. All other solvents and reagents were used as received. 1,1,3,3-Tetramethylisoindolin-2-yloxy (TMIO) was prepared as described[15] (see Supporting Information). Photolyses of diazo ketones were carried out in a Rayonet reactor using lamps of wavelengths chosen based on the absorption spectra of the substrates and products.

1-Diazo-6-hepten-2-one (8a).[13a] 5-Hexenoyl chloride (0.61 g, 5.0 mmol) from the acid[13e] in 5 mL ether was added dropwise over 0.5 h to stirring cooled diazomethane (12.5 mmol, 2.5 equiv.) in 60 mL of ether, and left stirring cold for an additional 2 h. The excess diazomethane was evaporated and quenched in acetic acid, and the solution was concentrated. Chromatography (30% EtOAc/hexane) gave **8a** (0.42 g, 61%) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.73 (q, 2), 2.08 (dt, 2), 2.33 (t, 2), 4.97−5.06 (m, 2), 5.22 (s, 1), 5.70−5.82 (m, 1). IR (pentane) 2106, 1666 cm^{-1}.

Reaction of 4-Pentenylketene (4a) with TEMPO. 1-Diazo-6-hepten-2-one (10 mg, 0.072 mmol) in 25 mL of pentane was photolyzed 1 min with 250 nm light to give **4a**, IR 2120.5

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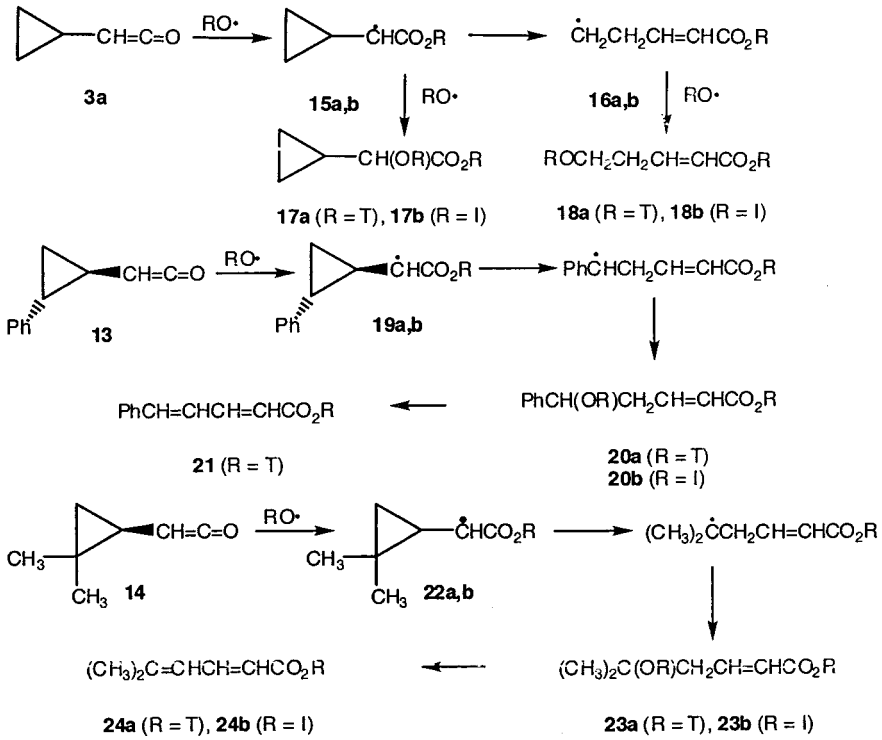
Scheme 1



cm^{-1}. TEMPO (30 mg, 0.18 mmol) was added and the solution stirred 31 h at 25 °C. Chromatography (15% EtOAc/hexane) gave **11a** (19 mg, 63%). ^{1}H NMR ($CDCl_3$) δ 1.02−2.11 (m, 42), 4.47 (t, 1), 4.93−5.03 (m, 2), 5.22 (s, 1), 5.75−5.82 (m, 1). ^{13}C NMR ($CDCl_3$) δ 17.2, 20.8, 34.0, 40.7, 60.5, 83.6, 115.1, 138.6, 149.9, 171.9. EIMS *m*/*z* 423 (MH^+), 266, 156, 140, 97, 83. IR (pentane) 1785 cm^{-1}.

Isomerization of 11a. A solution of **11a** (20 mg, 0.047 mmol) in 4 mL t-BuOH under argon was heated 24 h at 130 °C. The solvent was evaporated and chromatography (9/1 $CHCl_3$/MeOH) gave **12a** (15 mg, 74%) as a 55/45 *cis*/*trans* mixture. ^{1}H NMR ($CDCl_3$) δ 0.9−2.5 (m, 48), 2.62−2.70 (m, 1), 2.86−2.93 (m 1), 3.68−3.76 (m, 2), 3.86−3.94 (m, 2). ^{13}C NMR ($CDCl_3$) δ 17.26, 17.3, 20.6, 20.8, 25.6, 28.8. 29.3, 29.9, 30.1, 30.4, 33.0, 33.5, 39.9, 40.0, 42.7, 42.73, 45.8, 48.5, 60.1, 60.4, 80.4, 95.7, 178.1. EIMS *m*/*z* 423, 284, 185, 142, 93. IR (pentane) 1749 cm^{-1}.

1-Diazo-7-phenyl-6-hepten-2-one (8b).[13b] 6-Phenyl-5-hexenoyl chloride (0.80 g, 4.0 mmol) in 5 mL ether and added over 0.5 h to a stirring cooled solution of diazomethane (0.125 mol) in 60 mL of ether and stirred cold 2 h. Excess diazomethane was evaporated and quenched in acetic acid, and the remaining solution was concentrated. Chromatography (3/7 EtOAc/hexane) gave **8b** (87/13 *E*/*Z* mixture, 0.65 g, 75%) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.84 (q, 2), 2.25 (dt, 2), 2.37 (t, 2), 5.22 (s, 1), 5.63 (m, 1), 6.19 (m, 1), 6.40 (m, 1), 7.30−7.33 (m, 5). IR (pentane) 2106, 1666 cm^{-1}.

Reaction of 5-Phenyl-4-pentenylketene (9) with TEMPO. 1-Diazo-7-phenyl-6-hepten-2-one (10 mg, 0.047 mmol) in 25 mL of pentane was photolyzed for 1 min with 250 nm light to give **9** (IR 2119 cm^{-1}). TEMPO (15 mg, 0.096 mmol) was added and the solution was stirred 24 h at 25 °C. Chromatography with CH_2Cl_2 to remove excess TEMPO and then with Et_2O gave **11b** (94/6 *E*/*Z* mixture, 16 mg, 67%). ^{1}H NMR ($CDCl_3$) δ 1.10−2.31 (m, 42), 4.53 (t, 1), 5.63 (m, 1), 6.13−6.27 (m, 1), 6.39−6.44 (m, 1), 7.29−7.34 (m, 5). ^{13}C NMR ($CDCl_3$) δ 24.4, 32.6, 33.5, 34.2, 39.8, 40.4, 82.2, 126.1, 126.5, 128.4, 130.3, 171.9. EIMS (*m*/*z*) 499 (MH^+), 360, 342, 185, 156, 140, 126, 98, 84, 69, 58, 41. IR (pentane) 1772 cm^{-1}.

Generation of Phenylketene (1a) and Trapping with TMIO. Diazoacetophenone (15 mg, 0.10 mmol) in 20 mL pentane was irradiated for 15 min with 300 and 350 nm light, and TMIO (55 mg, 0.29 mmol) was added at room temperature and stirred 16 h. The pentane was evaporated and chromatographed (5% EtOAc/hexane) yielding **25a** (15 mg, 0.030 mmol, 30%) mp 133−135 °C. ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 3), 1.21 (s, 3), 1.37 (s, 6), 1.51 (s, 3), 1.59 (s, 3), 1.64 (s, 3), 5.49 (s, 1), 7.0−7.6 (m, 13). ^{13}C NMR ($CDCl_3$) δ 25.2, 25.4, 29.9, 30.3, 67.9, 68.2, 86.6, 121.4, 121.6, 127.2, 127.3, 127.5, 127.6, 128.5, 128.6, 137.2, 143.9, 144.5, 145.0, 171.4. IR ($CDCl_3$) 1779 cm^{-1}. EIMS *m*/*z* 499 (1), 308 (5), 190 (100), 174 (59). HREIMS *m*/*z* calcd for $C_{32}H_{39}N_2O_3$ 499.2961, found 499.2947.

Generation of *n*-Butylketene (1b) and Trapping with TMIO. 1-Diazo-2-hexanone (20 mg, 0.16 mmol) in 10 mL of pentane was irradiated for 10 min with 250 nm light and then TMIO (86 mg, 0.45 mmol) was added at room temperature and the solution stirred for 18 h. The pentane was evaporated and the residue chromatographed (20% EtOAc/hexane) yielding **25b** (31 mg, 0.067 mmol, 38%) as pale yellow crystals, mp 122−125 °C. ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3, J = 5.7 Hz), 1.36−1.70 (m, 28), 1.82−2.04 (m, 2), 4.61 (t, 1, J = 4.8 Hz), 7.1−7.4 (m, 8). ^{13}C NMR ($CDCl_3$) δ 13.9, 14.1, 15.3, 22.6, 22.8, 25.3, 25.7, 27.6, 28.8, 30.0, 31.3, 31.6, 32.7, 65.8, 68.2, 68.3, 68.4, 82.9, 121.3, 121.5, 127.2, 127.3, 127.5, 173.2. IR ($CDCl_3$) 1776 cm^{-1}. EIMS *m*/*z* 479 (0.02), 288 (16), 190 (19), 174 (100). HREIMS *m*/*z* calcd for $C_{30}H_{43}N_2O_3$ 479.3274, found 479.3262.

Generation of Cyclopropylketene (3a) and Trapping with TEMPO. Cyclopropyl diazomethyl ketone (**8c**, 86 mg, 0.78 mmol) in 60 mL pentane was irradiated for 10 min with 250 nm light and TEMPO (265 mg, 1.7 mmol) was added at room temperature and the solution stirred for 18 h. The pentane was evaporated and excess TEMPO was removed by Kugelrohr distillation. Chromatography (CH_2Cl_2) gave **17a** (22 mg, 0.06 mmol, 7%) as an orange oil. Further elution (2% MeOH in CH_2Cl_2) gave a mixture of **18a**-*E*/*Z* (32 mg, 0.08 mmol, 11%) as an orange oil. **17a**: ^{1}H NMR ($CDCl_3$) δ 0.30−0.38 (m, 1), 0.52−0.58 (m, 1), 0.64−0.78 (m, 2), 1.1−1.8 (m, 37), 3.64 (d, 2, J = 9.4 Hz). ^{13}C NMR ($CDCl_3$) δ 2.0, 7.9, 14.3, 16.8, 17.0, 19.9, 20.2, 20.4, 20.5, 31.7, 31.8, 33.6, 34.4, 39.0, 40.1, 40.2, 59.6, 59.9, 60.0, 60.5, 89.0, 170.1. IR ($CDCl_3$) 1756 cm^{-1}. EIMS *m*/*z* 395 (0.05), 238 (20), 156 (76), 140 (100). HREIMS *m*/*z* calcd for $C_{23}H_{43}N_2O_3$ 395.3274, found 395.3258. *E*-**18a**: ^{1}H NMR ($CDCl_3$) δ 1.04−1.76 (m, 36), 2.40−2.46 (m, 2), 3.82−3.88 (m, 2), 5.89 (d, 1, J = 15.5 Hz), 7.02−7.10 (m, 1). ^{13}C NMR ($CDCl_3$) δ 17.2, 17.3, 20.3, 20.8, 29.3, 30.4, 32.1, 32.15, 33.3, 36.8, 39.2, 39.8, 45.4, 55.8, 59.9, 60.0, 60.3, 74.7,

121.7, 146.5, 166.6. IR ($CDCl_3$) 1732 cm^{-1}. EIMS *m/z* 395 (4), 238 (66), 156 (23), 140 (100). HREIMS *m/z* calcd for $C_{23}H_{43}N_2O_3$ 395.3274, found 395.3277. *Z*-**18a**: ^1H NMR ($CDCl_3$) δ 1.04−1.76 (m, 36), 2.88−2.95 (m, 2), 3.82−3.88 (m, 2), 5.85−5.95 (d, 1), 6.36−6.42 (m, 1). ^{13}C NMR ($CDCl_3$) δ 17.2, 17.3, 20.3, 20.8, 29.3, 30.4, 32.1, 32.15, 33.3, 36.8, 39.2, 39.8, 45.4, 55.8, 59.9, 60.0, 60.3, 75.4, 119.2, 147.8, 177.9. Structural assignments confirmed by COSY, HSQC, TOCSY, HMBC.

Generation of Cyclopropylketene (3a) and Trapping with TMIO. Cyclopropyl diazomethyl ketone (**8c**, 18 mg, 0.16 mmol) in 20 mL isooctane was irradiated for 7 min with 250 nm light and TMIO (62 mg, 0.33 mmol) was added and the solution was stirred at 50 °C for 20 h. After evaporation of the isooctane chromatography (5% EtOAc/hexane) gave **17b**, mp 139−140 °C (21 mg, 0.046 mmol, 29%), and further elution with CH_2Cl_2 afforded *E*-**18b**, mp 91−93 °C (6 mg, 0.012 mmol, 8%). **17b**: ^1H NMR ($CDCl_3$) δ 0.54−0.98 (m, 4), 1.26−1.70 (m, 24), 3.87 (d, 1, J = 9.3 Hz), 7.10−7.40 (m, 10). ^{13}C NMR ($CDCl_3$) δ 2.2, 5.3, 13.7, 25.4, 25.6, 28.7, 29.6, 30.1, 31.4, 68.0, 68.4, 68.7, 87.3, 121.3, 121.5, 121.6, 127.2, 127.3, 127.5, 143.9, 144.7, 145.3, 172.5. IR ($CDCl_3$) 1778 cm^{-1}. EIMS *m/z* 463 (0.02), 272 (17), 190 (50), 174 (100). HREIMS *m/z* calcd for $C_{29}H_{39}N_2O_3$ 463.2961, found 463.2945. *E*-**18b**: ^1H NMR ($CDCl_3$) δ 1.20−1.64 (m, 24), 2.56−2.68 (m, 2), 4.08 (t, 2, J = 5.7 Hz), 6.18 (d, 1, J = 12.0 Hz), 7.04−7.10 (m, 9). ^{13}C NMR ($CDCl_3$) δ 25.4, 28.8, 32.4, 67.3, 68.3, 75.0, 121.0, 121.4, 121.5, 127.2, 127.6, 144.1, 145.0, 147.2, 167.0. IR ($CDCl_3$) 1744 cm^{-1}. EIMS *m/z* 463 (6), 272 (25), 190 (13), 174 (56). HREIMS *m/z* calcd for $C_{29}H_{39}N_2O_3$ (MH^+) 463.2961, found 463.2923.

Generation of 2-Phenyl-1-cyclopropylketene (13) and Trapping with TEMPO. *E*-2-Phenyl-1-cyclopropyl diazomethyl ketone (**8d**,[16a] 18 mg, 0.097 mmol) in 20 mL pentane was irradiated 7 min with 250 nm light, and TEMPO (310 mg, 2.0 mmol) was added at room temperature and the solution was stirred 18 h. The pentane was evaporated and excess TEMPO was removed by Kugelrohr distillation. Chromatography (5% EtOAc/hexane) gave the elimination product 2-*Z*-4-*E*-**21a** as a white solid, mp 82−84 °C, *Z*-**20a** as an orange oil (6.5 mg, 0.014 mmol, 14%), and a mixture of *E*,*E*−**21a** and *E*-**20a** (25 mg, 0.053 mmol, 55%) as an orange oil that were separated on further chromatography. *Z*-**20a**: ^1H NMR ($CDCl_3$) δ 0.66 (bs, 3), 0.96−1.82 (m, 33), 3.28−3.84 (m, 1), 3.50−3.64 (m, 1), 4.83 (dd, 1, J = 7.2, 4.8 Hz), 5.70−5.90 (m, 1), 6.06−6.22 (m, 1), 7.2−7.6 (m, 5). ^{13}C NMR ($CDCl_3$) δ 16.4, 16.5, 19.8, 20.0, 31.2, 33.3, 33.9, 35.0, 38.4, 39.8, 59.2, 85.1, 118.4, 126.5, 127.0, 127.3, 129.1, 142.0, 145.7. IR ($CDCl_3$) 1742 cm^{-1}. EIMS *m/z* 471 (3), 314 (7), 156 (15), 140 (100). *E*-**20a**: ^1H NMR ($CDCl_3$) δ 0.66 (bs, 3), 0.96−1.82 (m, 33), 2.64−2.82 (m, 1), 2.94−3.08 (m, 1), 4.81 (dd, 1, J = 5.1, 3.3 Hz), 5.70 (d, 1, J = 16.5 Hz), 6.76−6.88 (m, 1), 7.2−7.6 (m, 5). ^{13}C NMR ($CDCl_3$) δ 16.5, 16.7, 20.1, 29.3, 31.4, 38.5, 39.2, 40.0, 59.6, 85.3, 121.7, 126.9, 127.0, 127.6, 142.0, 144.8. IR ($CDCl_3$) 1731 cm^{-1}. EIMS *m/z* 471 (0.5), 314, 156 (30), 140 (100). *E*,*Z*-**21a**: ^1H NMR ($CDCl_3$) δ 1.10 (s, 6), 1.19 (s, 6), 1.4−1.8 (m, 6), 5.79 (d, 1, J = 7.5 Hz), 6.76−6.86 (m, 2), 7.28−7.36 (m, 3), 7.46−7.56 (m, 2), 8.22 (dd, 1, J = 10.1, 8.4 Hz). ^{13}C NMR ($CDCl_3$) δ 17.0, 20.6, 32.0, 39.1, 59.9, 115.6, 125.2, 127.4, 128.7, 128.9, 136.3, 141.1, 145.3. IR ($CDCl_3$) 1735 cm^{-1}. EIMS *m/z* 313, 157 (100). HREIMS *m/z* calcd for $C_{20}H_{27}NO_2$ 313.2042, found 313.2043. *E*,*E*-**21a** (mp 153−156 °C): ^1H NMR ($CDCl_3$) δ 1.09 (s, 6), 1.20 (s, 6), 1.4−1.8 (m,6), 6.04 (d, 1, J = 11.7 Hz), 6.86−6.94 (m, 2), 7.3−7.6 (m, 6). ^{13}C NMR ($CDCl_3$) δ 17.0, 20.6, 31.9, 38.0, 60.1, 119.8, 126.0, 127.2, 126.2, 128.8, 129.0, 136.0, 140.4, 144.8. IR ($CDCl_3$) 1728 cm^{-1}. EIMS *m/z* 313 (0.1), 157 (100), 156. HREIMS *m/z* calcd for $C_{20}H_{27}NO_2$ 313.2042, found 313.2047.

Generation of 2-Phenylcyclopropylketene (13) and Trapping with TMIO. *E*-2-Phenyl-1-cyclopropyl diazomethyl ketone (**8d**,[16a] 20 mg, 0.11 mmol) in 20 mL pentane was irradiated for 7 min with 250 nm light and TMIO (51 mg, 0.27 mmol) was added and the solution stirred 20 h at room temperature. After evaporation of the pentane, chromatography (5% EtOAc/hexane) yielded *Z*-**20b** (8 mg, 0.015 mmol, 14%) as pale white crystals, mp 82−84 °C, and elution with CH_2Cl_2 afforded *E*-**20b** (15 mg, 0.028 mmol, 25%) as pale white crystals, mp 111−113 °C. *E*-**20b**: ^1H NMR ($CDCl_3$) δ 0.82 (s, 3), 1.24−1.32 (m, 6), 1.38−1.54 (m, 12), 1.66 (s, 3), 2.68−2.80 (m, 1), 3.04−3.16 (m, 1), 4.90 (t, 1, J = 14.6 Hz), 6.12 (d, 1, J = 14.4 Hz), 6.98−7.52 (m, 14). ^{13}C NMR ($CDCl_3$) δ 25.2, 25.7, 28.8, 29.4, 30.0, 39.5, 68.3, 86.5, 121.3, 121.5, 121.6, 121.7, 127.6, 127.65, 128.0, 128.2, 142.3, 144.0, 144.7, 145.1, 146.4, 166.8. IR ($CDCl_3$) 1740 cm^{-1}. EIMS *m/z* 539 (0.01), 348 (8), 190 (40), 174 (17), 157 (100). HREIMS *m/z* calcd for $C_{35}H_{43}N_2O_3$ (MH^+) 539.3274, found 539.3257. *Z*-**20b**: ^1H NMR ($CDCl_3$) δ 0.83 (s, 3), 1.24−1.70 (m, 21), 3.24−3.36 (m, 1), 3.54−3.70 (m, 1), 4.94 (bs, 1), 6.06 (d, 1, J = 10.8 Hz), 6.36−6.46 (m, 1), 6.8−7.4 (m, 13). ^{13}C NMR ($CDCl_3$) δ 25.3, 25.4, 25.7, 28.8, 29.5, 30.0, 35.7, 68.1, 86.6, 119.0, 121.3, 121.5, 121.6, 127.1, 127.2, 127.5, 127.9, 128.1, 144.0, 147.7, 166.7. IR ($CDCl_3$) 1741 cm^{-1}. EIMS *m/z* 539 (0.05), 348 (4), 190 (21), 174 (16), 157 (100). HREIMS *m/z* calcd for $C_{35}H_{43}N_2O_3$ (MH+) 539.3274, found 539.3294.

Generation of 2,2-Dimethylcyclopropylketene (14) and Trapping with TEMPO. 2,2-Dimethylcyclopropyl diazomethyl ketone (**8e**,[16b] 32 mg, 0.23 mmol) in 40 mL of pentane was irradiated for 4 min with 250 nm light and TEMPO (910 mg, 5.83 mmol) was added at room temperature and the solution stirred for 24 h. The pentane was evaporated and excess TEMPO removed by Kugelrohr distillation, and chromatography (10% EtOAc/hexane) gave *Z*-**24a** (4 mg, 0.015 mmol, 6%) as white needles (mp 105−108 °C) and then *E*-**24a** (11 mg, 0.041 mmol, 18%) as white crystals (mp 68−71 °C). *Z*-**24a**: ^1H NMR ($CDCl_3$) δ 1.06 (s, 6), 1.16 (s, 6), 1.2−1.7 (m, 6), 1.85 (s, 3), 1.9 (s, 3), 5.55−5.65 (bd, 1), 6.85−6.95 (m, 2). ^{13}C NMR ($CDCl_3$) δ 17.3, 18.5, 20.9, 27.2, 32.2, 39.3, 60.1, 113.2, 122.6, 141.2, 146.3, 180.4. IR ($CDCl_3$) 1734 cm^{-1}. EIMS *m/z* 266 (9), 156 (20), 140 (36), 109 (100), 81 (100). HREIMS *m/z* calcd for $C_{16}H_{27}NO_2$ 265.2042, found 265.2050. *E*-**24a**: ^1H NMR ($CDCl_3$) δ 1.06 (s, 6), 1.17 (s, 6), 1.4−1.8 (m, 6), 1.88 (s, 3), 1.9 (s, 3), 5.80 (d, 1, J = 15.0 Hz), 6.01 (d, 1, J = 11.4 Hz), 7.62 (dd, 1, J = 13.2, 11.4 Hz). ^{13}C NMR ($CDCl_3$) δ 16.9, 18.9, 20.4, 26.4, 31.7, 38.8, 59.9, 116.8, 123.7, 141.3, 146.2, 167.8. IR ($CDCl_3$) 1732 cm^{-1}. EIMS *m/z* 265 (2), 156 (5), 109 (100), 81 (31). HREIMS *m/z* calcd for $C_{16}H_{27}NO_2$ 265.2042, found 265.2047.

Generation of 2,2-Dimethylcyclopropyl Ketene (14) and Trapping with TMIO. 2,2-Dimethyl-1-cyclopropyl diazomethyl ketone (**8e**,[16b] 30 mg, 0.22 mmol) in 40 mL pentane was irradiated for 4 min with 250 nm light and TMIO (104 mg, 0.55 mmol) was added at room temperature and the solution stirred for 24 h. After evaporation of the pentane chromatography (15% EtOAc /hexane) gave *Z*-**24b** (5 mg, 0.015 mmol, 7%) as a pale white solid (mp 87−90 °C) and *E*-**24b** (34 mg, 0.12 mmol, 53%) as a pale white solid (mp 75−77 °C). *Z*-**24b**: ^1H NMR ($CDCl_3$) δ 1.41 (bs, 6), 1.49 (bs, 6), 1.88 (s, 3), 1.92 (s, 3), 5.8 (m, 1), 6.9−7.3 (m, 1), 7.08−7.16 (m, 4), 7.2−7.3 (d, 1). ^{13}C NMR ($CDCl_3$) δ 18.5, 25.1, 25.7, 27.1, 29.2, 29.9, 68.4, 112.4, 121.8, 122.6, 127.8, 141.8, 144.5, 147.5, 167.6. IR ($CDCl_3$) 1739 cm^{-1}. EIMS *m/z* 300 (1), 190 (19), 109 (100), 81 (29). HREIMS *m/z* calcd for $C_{19}H_{26}NO_2$ 300.1964, found 300.1972. *E*−**24b**: ^1H NMR ($CDCl_3$) δ 1.46 (bs, 6), 1.52 (bs, 6), 1.93 (s, 3), 1.95 (s, 3), 6.02−6.14 (m, 2), 7.12−7.2 (m, 2), 7.26−7.36 (m, 2), 7.73 (dd, 1, J = 14.1, 11.4 Hz). ^{13}C NMR ($CDCl_3$) δ 18.8, 25.2, 26.4, 28.6, 68.0, 115.8, 121.3, 123.7, 127.4, 142.1, 143.9, 146.8, 168.6. IR ($CDCl_3$) 1732 cm^{-1}. EIMS *m/z* 299 (0.5), 190 (5), 109 (100), 81 (35). HREIMS *m/z* calcd for $C_{19}H_{25}NO_2$ 299.1885, found 299.1882.

Kinetics of Phenylketene (1a) and TMIO. Ketene **1a** (0.020 mL of a 0.085 mM solution from 5 min irradiation of diazoacetophenone with 300 and 350 nm light) was injected into 1.2 mL of a 0.253 to 1.12 mM TMIO solution. The decrease of the absorption at 249 nm gave good first-order kinetics.

Kinetics of *n*-Butylketene (1b) and TMIO. 1-Diazo-2-hexanone (0.250 mL of a 0.0190 M solution in isooctane) was

(16) (a) Feldman, K. S.; Simpson, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 4878−4886. (b) See Supporting Information.

irradiated in a UV cell for 4 min at 250 nm to form **1b**. This was pipetted into a 1.2 mL UV cell containing 0.2−0.5 mL of a 0.106 M TMIO solution. For the 0.2 mL TMIO solution 0.167 mL of diazoketone solution was used, and isooctane was added to give final volumes of 0.75 mL. The decrease in the absorption at 355 nm gave good first-order kinetics.

IR Spectra of Ketenes. Cold solutions of the ketenes were quickly transferred to an IR cell for observation of the ketene bands.

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Supporting Information Available: Experimental details and ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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