

Aminoxyl radical addition to arylketenes[†]

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ABSTRACT: Kinetic studies of the addition of the aminoxyl radical TEMPO (2,2,6,6-tetramethylpiperidinylaminoxyl, TO·) to the 4-substituted phenylketenes **8** (4-RC₆H₄CH=C=O, R=NO₂, CN, Cl, H, CH₃, CH₃O) and to 3-pyridylketene (**15**) reveal a correlation of log*k*₂(TEMPO) with the Hammett sigma parameters of the substituents (including the aza substituent of **15**), with rho = 1.58 (*r* = 0.94). A better correlation is obtained with the rate constants for hydration of the same substrates: log*k*₂(TEMPO) = 1.64log*k*(H₂O) – 5.76 (*r* = 0.98). These results fit within a previously established correlation of ketene hydration reactivity with aminoxyl radical reactivity, and confirm that the reactivity of TEMPO in additions to ketenes is dominated by the nucleophilic character of the aminoxyl oxygen, with a strong trend of increasing reactivity for more electrophilic ketenes. Copyright © 2006 John Wiley & Sons, Ltd.

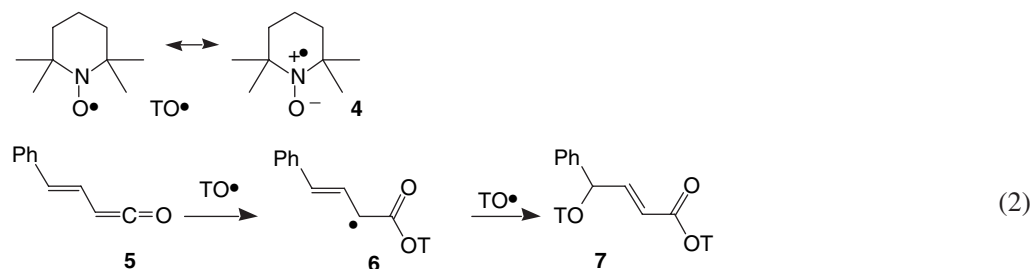
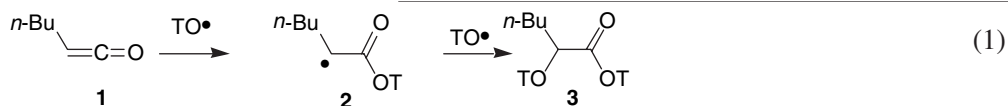
KEYWORDS: ketenes; TEMPO; free radical addition; substituent effects

INTRODUCTION

Previous studies of the reactivity of ketenes with the aminoxyl radical 2,2,6,6-tetramethylpiperidinylaminoxyl (TEMPO, TO·) have provided convincing evidence that this reaction proceeds by initial oxygen attack by TEMPO in the ketene plane on the carbonyl carbon to give enolic radical intermediates which are ordinarily captured by addition of a second TEMPO radical at the enolic carbon [Eqn (1)].¹ For ketenes with unsaturated substituents such as vinyl or alkynyl groups conjugate addition may occur [Eqn (2)].^{1c–e}

reactivity with conjugating ketene substituents,¹ conjugate additions to substrates with unsaturated substituents Eqn (2)],^{1c,d} cyclopropylcarbinyl radical ring opening in substrates with cyclopropyl substituents,^{1f} trapping by oxygen of stabilized enolic radicals from diarylketenes,^{1b} and a correlation of ketene reactivity with aminoxyl reactivity compared to hydration reactions involving data for 16 ketenes Eqn (3)].^{1c,d,h}

$$\log k(\text{TEMPO}) = 1.18 \log k(\text{H}_2\text{O}) - 4.45 (r = 0.94) \quad (3)$$



Evidence for this reaction pathway includes computational studies,^{1b,g} the large kinetic accelerations of the

This correlation, however, may seem surprising, in that radicals are electron deficient species, and might be expected to be electrophilic in character, and not nucleophilic. However, nitroxyl radicals are often named as ‘nitroxides,’ emphasizing the high-electron density on oxygen, as shown in the resonance structure **4**. Indeed detailed study of the factors controlling

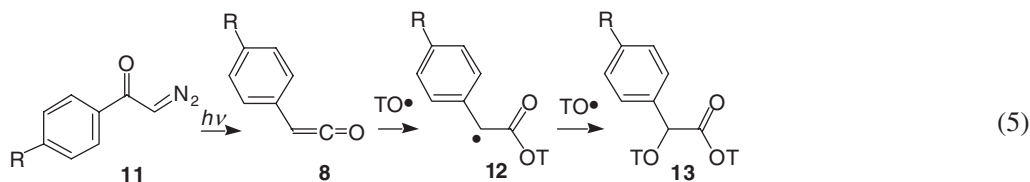
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reactivity in additions of carbon centered radicals to alkenes emphasizes that the variable polar character of different types of radicals plays a major role in these processes.²

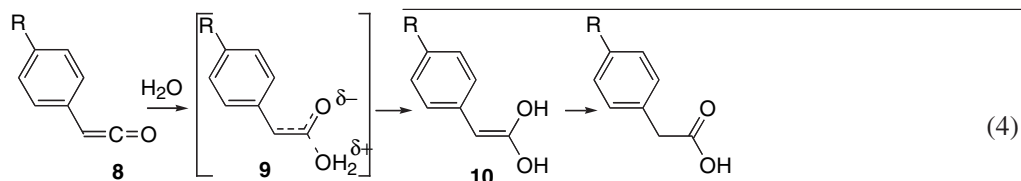
One of the most useful criteria for the interpretation of addition reactions to alkenes has been the effect of aryl substituents on the reactivity of styrenes, and this criterion has been especially applied to electrophilic additions, including styrene protonation.³ Arylketenes may be considered as a special class of styrenes, and indeed the reported correlation of the hydration reactivity of substituted phenylketenes **8** using Hammett sigma parameters with a slope $\rho = 1.2$ has been taken as strong evidence that these reactions are polar additions with nucleophilic attack on carbonyl carbon with

substituted benzoyl chlorides with diazomethane in ether. Photolysis of the diazo ketones in hexane with 254 or 300 nm light gave the corresponding ketenes **8**, identified using conventional FTIR by their distinctive absorption at 2116, 2116, 2119, 2123, and 2123 cm^{-1} , respectively [Eqn (5)]. Qualitatively it was apparent that the ketenes were progressively shorter lived as the substituents became increasingly more electron withdrawing. Thus, for the 4-MeO and 4-Me substituents the IR absorptions were strong and relatively long-lived, while those for the 4-NO₂ and 4-CN substituents were weaker, and transient. The UV spectra of the ketenes **8** in isoctane were also measured, and minimum values of the extinction coefficients were estimated based on the assumption that the diazo ketones **11** were completely converted to ketenes **8** (Table 1).



zwitterionic transition states **9** leading to acid enol intermediates **10**, which lead to the carboxylic acids [Eqn (4)].⁴ This result argues against an earlier proposal that these were concerted reactions with rate limiting proton transfer to C(2) through cyclic transition states, forming the acids directly.^{4c-d} The present study reports the examination of the influence of different substituted aryl groups on the addition of TEMPO to arylketenes to further elucidate the nature of the transition state of this reaction.

Product studies of the reactions of the ketenes **8** with TEMPO in hexane were carried out by adding TEMPO to solutions of the ketenes generated by photolysis of the diazo ketones in hexane for the 4-MeO, 4-Me, and 4-Cl substituted derivatives, while for the 4-CN and 4-NO₂ substituted compounds photolysis was carried out in the presence of TEMPO for in situ trapping. The 1,2-diaddition products **13** were isolated in 25–49% yields [Eqn (5)]. 3-Pyridylketene (**15**) was also generated by photochemical Wolff rearrangement of the diazo ketone



RESULTS

4-Substituted diazoacetylbenzenes **11** with MeO, Me, Cl, CN, and NO₂ substituents were prepared by reaction of the

14, as we have done previously for examination of its reactivity in amination⁵ and hydration,^{5b} and reacted with TEMPO to give the 1,2-diaddition product **16** [Eqn (6)]. This substrate may be included in a Hammett type correlation by using a sigma constant for the 3-aza group of 0.55.^{5c,d}

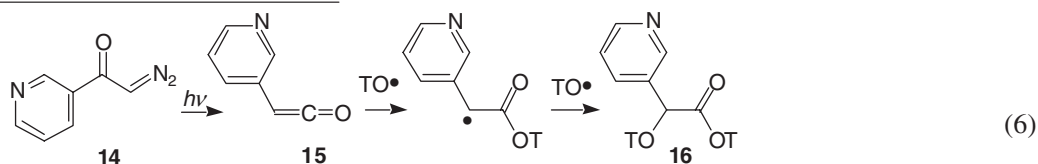


Table 1. Ketenyl IR absorption and UV spectra of arylketenes **8** and **15**

R	IR (cm ⁻¹) ^a	UV (λ _{max} nm), ε (isooctane) ^b
MeO (8a)	2116	251 (6.3 × 10 ³), 390 (25)
Me (8b)	2116	250 (1.8 × 10 ⁴), 380 (120)
H (8c)	2118	248 (1.2 × 10 ⁴), 378 (47)
Cl (8d)	2119	255 (1.4 × 10 ⁴), 370 (72)
CN (8e)	2123	218 (1 × 10 ⁴), 224 (1 × 10 ⁴), 273 (1.6 × 10 ⁴), 370 (93)
NO ₂ (8f)	2123	225 (5.4 × 10 ³), 261 (4 × 10 ³), 317 (7.4 × 10 ³)
Ar = 3-Pyridyl (15)	2123	250 (4.3 × 10 ³), 290 (7 × 10 ²)

^a Hexane.^b Minimum values of ε assuming complete conversion of the diazo ketenes to the ketenes.

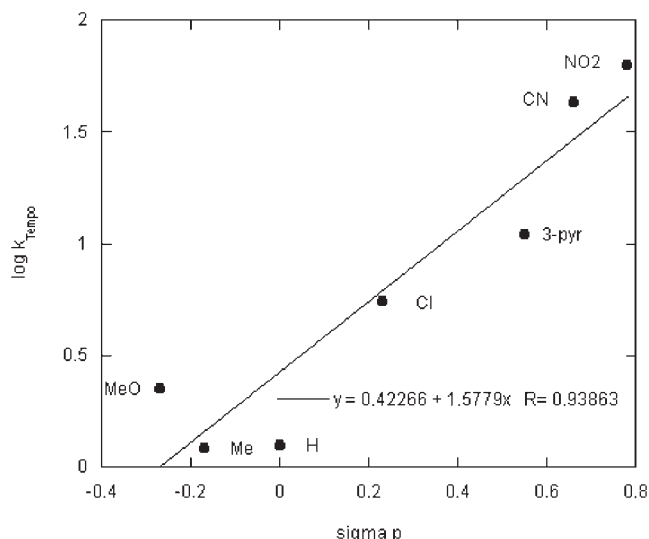
Rate constants were measured for the reaction of the 4-substituted phenylketenes **8** and for 3-pyridylketene (**15**) with different concentrations of excess TEMPO under pseudo first order conditions by measuring the decrease in the UV absorption of the ketenes as carried out previously,^{1c-h} and plots of the measured rate constants versus the TEMPO concentration gave second order rate constants, as reported in Table 2, together with previous results^{1c,d} for phenylketene (**8c**, R = H). Also included in Table 2 are the reported rate constants for hydration of these 4-substituted arylketenes, as measured by the change in conductivity of the solutions.^{6a} When the hydration of phenylketene (**8c**) is observed by UV spectroscopy, two processes are observed, conversion of the ketene to the acid enol, and conversion of the acid enol to the carboxylic acid.^{5e} The observed rate constants for generation of the carboxylic acids measured by conductivity should correspond closely to the rate constants for nucleophilic attack of water on the ketene.^{6a}

DISCUSSION

The rate constants for reaction of the 4-substituted phenylketenes **8** and 3-pyridylketene **15** with TEMPO

Table 2. Rate constants for TEMPO addition and for hydration of arylketenes **8** (4-RC₆H₄CH=C=O) and 3-pyridylketene (**15**)

R	Sigma ^a	k ₂ (TEMPO) 25°C, s ⁻¹ M ⁻¹	k(H ₂ O) s ^{-1b}
CH ₃ O (8a)	-0.27	2.26	4.5 × 10 ³
CH ₃ (8b)	-0.17	1.23	3.8 × 10 ³
H (8c) ^c	0.0	1.26	4.9 × 10 ³
Cl (8d)	0.23	5.55	9.6 × 10 ³
CN (8e)	0.66	43.4	2.56 × 10 ⁴
NO ₂ (8f)	0.78	63.6	4.95 × 10 ⁴
3-Py (15)	0.55 ^d	11.0	1.6 × 10 ^{4e}

^a Ref. ^{3c} unless noted.^b Ref. ^{6a}, unless noted.^c Refs. ^{1c,d}.^d Ref. ^{5c,d}.^e Ref. ^{5b}.**Figure 1.** Plot of log₂(TEMPO) versus sigma (para) constants for arylketenes **8** and **15**

vary by a factor of 52 for the different substituents, and give a correlation with the Hammett sigma constants (Fig. 1) with a slope of 1.6 and a correlation coefficient $r = 0.94$ [Eqn (7)]. This compares with the rho value of 1.2 found for the rate constants for hydration of the phenylketenes **8** with the sigma constants.⁶ The correlation coefficient of 0.94 is only fair, but the trend in reactivity with higher reactivity for the ketenes with the more strongly electron withdrawing substituents is unmistakable, and agrees with the previously found parallel between ketene reactivity with nitroxyl radicals and with water, showing the nucleophilic character of the reaction.^{1c-h}

$$\log k_2(\text{TEMPO}) = 1.56\sigma + 0.42 \quad (r = 0.94) \quad (7)$$

Correlation of log₂ for reaction of ketenes with TEMPO with log₂ for reaction with water (Fig. 2) gives a better correlation, with a correlation coefficient of 0.98 [Eqn (8)]. This result confirms the utility of the study of arylketenes for the examination of the parallel between hydration reactions and TEMPO addition, and shows the strong nucleophilic character of the aminoxyl radical in this reaction. The formation of radical intermediates in these reactions of TEMPO with ketenes is confirmed by the addition of two TEMPO molecules, the ring opening of cyclopropylcarbinyl intermediates, and the reaction of the intermediates with molecular oxygen.^{1b}

$$\begin{aligned} \log k_2(\text{TEMPO}) \\ = 1.64 \log k(\text{H}_2\text{O}) - 5.76 \quad (r = 0.98) \quad (8) \end{aligned}$$

A new correlation of rate constants for ketene reactions with TEMPO and with water including the previous results and the results for the reaction of the arylketenes measured is given in Fig. 3 [Eqn (9)]. This includes 22

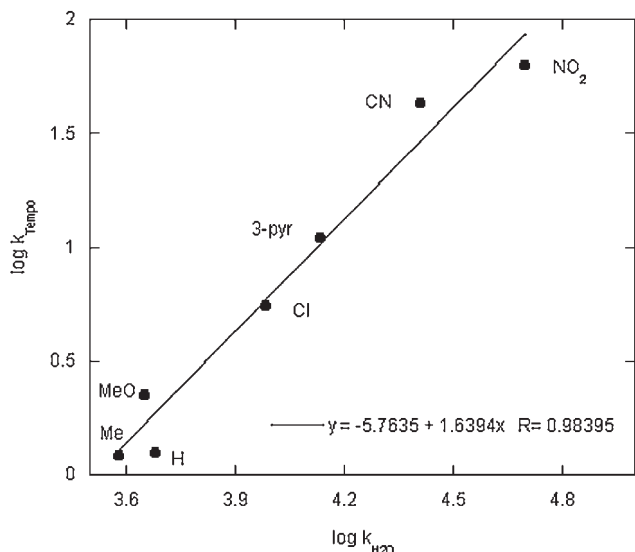


Figure 2. Plot of $\log k_2(\text{TEMPO})$ versus $\log k(\text{H}_2\text{O})$ for arylketenes **8** and **15**

ketenes, and covers a range of 10^7 in hydration reactivity, and 10^9 in reactivity with TEMPO.

$$\begin{aligned} \log k_2(\text{TEMPO}) \\ = 1.22 \log k(\text{H}_2\text{O}) - 4.93 \quad (r = 0.94) \end{aligned} \quad (9)$$

A possible reason for the even greater variation in reactivity as a function of structure for the reaction with TEMPO than for the reaction with water is that in hydration reactions more than one water molecule participates, leading to an enol intermediate **10** by addition to the ketene carbonyl [Eqn (4)].^{4a,5e} In the addition of TEMPO an enolic radical intermediate is formed [Eqn (6)], and so there is more conjugation possible with the aryl substituent compared to the hydration reaction.

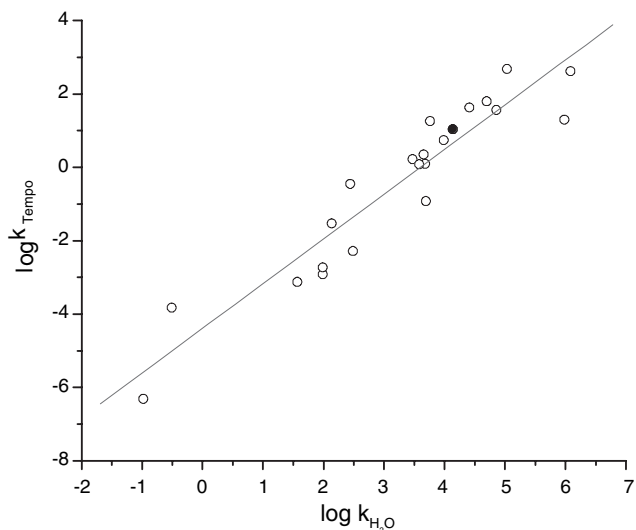


Figure 3. Plot of $\log k_2(\text{TEMPO})$ versus $\log k(\text{H}_2\text{O})$ for ketenes (filled circle is for 3-pyridylketene, **15**)

In summary, there is a correlation of the rate constants for addition of the aminoxyl radical TEMPO to arylketenes with the rate constants for hydration (Fig. 2), confirming the nucleophilic character of the aminoxyl radical. The results also fit with the general correlation of TEMPO reactivity with ketenes compared to hydration reactivity.

EXPERIMENTAL

The diazo ketones **11** are all known compounds,^{6a} and were prepared by reaction of the acyl chlorides with diazomethane.

Reaction of 4-Methoxyphenylketene (**8a**) with TEMPO

4-Methoxydiazoacetophenone (**11a**, 0.10 g, 0.57 mmol) and TEMPO (0.18 g, 1.2 mmol, 2.1 equiv) in hexane (75 mL) were photolyzed 1 h with 300 nm light and left stirring for 1 h at room temperature. The solution was concentrated and chromatographed using CH_2Cl_2 to give the bis(TEMPO) adduct **13a** (0.090 g, 0.20 mmol, 34%). ¹H NMR (400 MHz, CDCl_3) δ 0.47 (s, 3), 0.65 (s, 3), 0.84 (s, 3), 1.03 (s, 3), 1.12 (s, 3), 1.17 (s, 3), 1.23 (s, 3), 1.26 (s, 3), 1.36–1.62 (m, 12), 3.80 (s, 3), 5.28 (s, 1), 6.83 (d, 2, $J = 8.6$ Hz), 7.38 (d, 2, $J = 8.6$ Hz). ¹³C NMR (100 MHz, CDCl_3) 17.1, 17.3, 20.2, 20.8, 22.9, 31.2, 32.2, 33.7, 34.5, 39.4, 39.6, 40.5, 55.4, 60.1, 60.6, 87.3, 113.7, 128.5, 129.0, 129.7, 132.0. IR (CDCl_3) 1786 cm^{-1} . EIMS m/z 304 ($\text{M}^+ - \text{OT}$), 243, 165, 126, 83, 69, 56. HREIMS m/z calcd for $\text{C}_{18}\text{H}_{26}\text{NO}_3$ ($\text{M}^+ - \text{TO}$) 304.1912, found 304.1913. Photolysis of **11a** in hexane in the absence of TEMPO gave a solution displaying the ketenyl IR at 2116 cm^{-1} .

Reaction of 4-Methylphenylketene (**8b**) with TEMPO

4-Methyldiazoacetophenone (**11b**, 0.060 g, 0.38 mmol) in hexane (25 mL) was photolyzed 25 min with 254 nm light to generate the ketene **8b** (IR 2116 cm^{-1}). TEMPO (0.12 g, 0.79 mmol, 2.1 equiv) was added, and the solution was stirred for 2 h at room temperature. The solution was concentrated and chromatographed using CH_2Cl_2 to give the bis(TEMPO) adduct **13b** (0.080 g, 0.18 mmol, 47%). ¹H NMR (400 MHz, CDCl_3) δ 0.48 (s, 3), 0.69 (s, 3), 0.87 (s, 3), 1.06 (s, 3), 1.09 (s, 3), 1.16 (s, 3), 1.27 (s, 3), 1.30 (s, 3), 1.35–1.63 (m, 12), 2.36 (s, 3), 5.23 (s, 1), 7.15 (d, 2, $J = 8.1$ Hz), 7.36 (d, 2, $J = 7.9$ Hz). ¹³C NMR (100 MHz, CDCl_3) 17.0, 17.2, 20.2, 20.6, 21.3, 30.9, 32.0, 33.5, 34.2, 39.3, 39.8, 40.9, 59.2, 60.4, 87.5, 127.5, 128.8, 136.4, 137.5, 171.1. IR (CDCl_3) 1773 cm^{-1} . HREIMS m/z calcd for $\text{C}_{27}\text{H}_{45}\text{N}_2\text{O}_3$ (M^+) 445.3428, found 445.3424.

Reaction of 4-Chlorophenylketene (8d) with TEMPO

4-Chlorodiazooacetophenone (**11d**, 0.080 g, 0.44 mmol) in hexane (75 mL) was photolyzed 20 min with 254 nm light to generate the ketene **8d** (IR 2119 cm⁻¹). TEMPO (0.14 g, 0.92 mmol, 2.1 equiv) was added, and the solution was stirred for 2 h at room temperature. The solution was concentrated and chromatographed using 1:9 EtOAc/hexane to give the bis(TEMPO) adduct **13d** (0.10 g, 0.21 mmol, 49%). ¹H NMR (400 MHz, CDCl₃) δ 0.50 (s, 3), 0.67 (s, 3), 0.88 (s, 3), 1.06 (s, 3), 1.09 (s, 3), 1.14 (s, 3), 1.25 (s, 3), 1.29 (s, 3), 1.30–1.58 (m, 12), 5.28 (s, 1), 7.36 (d, 2, *J* = 8.5 Hz), 7.47 (d, 2, *J* = 8.3 Hz). ¹³C NMR (100 MHz, CDCl₃) 17.0, 17.2, 20.3, 20.7, 21.0, 31.1, 32.1, 33.5, 34.4, 39.2, 39.4, 40.4, 60.1, 60.6, 87.0, 128.9, 130.9, 138.0, 141.8, 175.2. IR (CDCl₃) 1777 cm⁻¹. HREIMS *m/z* calcd for C₂₆H₄₂ClN₂O₃ (M⁺) 465.2878, found 465.2862.

Reaction of 4-Cyanophenylketene (8e) with TEMPO

4-Cyanodiazooacetophenone (**11e**, 0.050 g, 0.29 mmol) and TEMPO (0.090 g, 0.61 mmol, 2.1 equiv) in hexane (100 mL) were photolyzed 25 min with 254 nm light and left stirring for 1 h at room temperature. The solution was concentrated and chromatographed using 3:7 EtOAc/hexane to give the bis(TEMPO) adduct **13e** (0.030 g, 0.066 mmol, 23%). ¹H NMR (400 MHz, CDCl₃) δ 0.44 (s, 3), 0.60 (s, 3), 0.84 (s, 3), 1.04 (s, 3), 1.08 (s, 3), 1.14 (s, 3), 1.26 (s, 3), 1.29 (s, 3), 1.37–1.65 (m, 12), 5.33 (s, 1), 7.63 (d, 2, *J* = 8.2 Hz), 7.67 (d, 2, *J* = 8.3 Hz). ¹³C NMR

(100 MHz, CDCl₃) 16.9, 17.0, 20.1, 20.3, 20.6, 31.0, 31.9, 33.3, 34.2, 39.2, 39.4, 40.3, 60.1, 60.6, 87.2, 111.9, 118.7, 128.3, 132.2, 144.6. IR (CDCl₃) 1776 cm⁻¹. HREIMS *m/z* calcd for C₂₇H₄₂N₃O₃ (M⁺) 456.3220, found 456.3222.

Reaction of 4-Nitrophenylketene (8f) with TEMPO

4-Nitrodiazooacetophenone (**11f**, 0.050 g, 0.26 mmol) and TEMPO (0.090 g, 0.55 mmol, 2.1 equiv) in hexane (100 mL) were photolyzed 35 min with 300 nm light and left stirring for 1 h. The solution was concentrated and chromatographed using CH₂Cl₂ to give the bis(TEMPO) adduct **13f** (0.030 g, 0.063 mmol, 25%). ¹H NMR (400 MHz, CDCl₃) δ 0.46 (s, 3), 0.61 (s, 3), 0.86 (s, 3), 1.06 (s, 3), 1.10 (s, 3), 1.16 (s, 3), 1.28 (s, 3), 1.31 (s, 3), 1.36–1.65 (m, 12), 5.40 (s, 1), 7.69 (d, 2, *J* = 8.6 Hz), 8.27 (d, 2, *J* = 8.6 Hz). ¹³C NMR (100 MHz, CDCl₃) 16.8, 17.0, 20.2, 20.3, 20.6, 31.1, 32.0, 33.3, 34.2, 39.2, 39.4, 40.3, 60.2, 60.7, 87.0, 123.7, 128.4, 130.7, 146.6, 169.7. IR (CDCl₃) 1789 cm⁻¹. EIMS *m/z* 476 (M⁺), 319 (M⁺-TO) 291, 270, 194, 164, 142, 89, 69, 56. HREIMS *m/z* calcd for C₂₆H₄₂N₃O₅ (M⁺) 476.3124, found 476.3124. Photolysis of **11a** in hexane in the absence of TEMPO gave a solution displaying the ketenyl IR at 2123 cm⁻¹.

Reaction of 3-Pyridylketene (3–15) with TEMPO

3-Diazoacetylpyridine (3–**14**, 14 mg, 0.095 mmol)^{5a} and TEMPO (31 mg, 0.200 mmol, 2.1 equiv) in hexane

Table 3. Kinetics of ketene reactions with TEMPO (isooctane, 25°C)

Ketene	Ketene [TEMPO] M × 10 ³	<i>k</i> _{obs} (s ⁻¹) × 10 ^{2a}	Ketene	[TEMPO] M × 10 ³	<i>k</i> _{obs} (s ⁻¹) × 10 ²
8a (R = MeO) ^b	4.11	0.934	8e ^e (R = CN) ^c	1.644	6.88
	3.29	0.766		0.822	4.05
	2.46	0.567		0.358	1.38
	1.644	0.373		0.286	1.14
	0.822	0.202		0.215	0.881
8b (R = Me) ^c	4.11	0.562	8f ^f (R = NO ₂) ^f	0.143	0.661
	3.29	0.485		0.358	2.89
	2.46	0.389		0.286	2.49
	1.644	0.274		0.215	2.12
	0.822	0.164		0.143	1.82
8d (R = Cl) ^d	4.11	2.72	3– 15 ^g (3-PyCH=C=O)	0.0715	1.010
	3.29	2.32		1.90	1.83
	2.46	1.62		3.81	2.97
	1.644	1.20		4.76	4.40
	0.821	0.994		5.71	5.31
			7.62	7.91	

^a Average of duplicate runs at each concentration.

^b *k*_{obs} = (2.26 ± 0.04) s⁻¹ M⁻¹ [TO] + (1.20 ± 1.01) × 10⁻⁴ s⁻¹.

^c *k*_{obs} = (1.23 ± 0.04) s⁻¹ M⁻¹ [TO] + (7.2 ± 1.0) × 10⁻⁴ s⁻¹.

^d *k*_{obs} = (5.50 ± 0.34) s⁻¹ M⁻¹ [TO] + (4.0 ± 1.0) × 10⁻³ s⁻¹.

^e *k*_{obs} = (43.4 ± 1.7) s⁻¹ M⁻¹ [TO] + (1.25 ± 12.3.) × 10⁻⁴ s⁻¹.

^f *k*_{obs} = (63.6 ± 4.6) s⁻¹ M⁻¹ [TO] + (6.9 ± 1.0) × 10⁻³ s⁻¹.

^g *k*_{obs} = (11.0 ± 1.13) s⁻¹ M⁻¹ [TO] + (7.33 ± 6.12) × 10⁻⁴ s⁻¹.

(30 mL) was degassed with argon over powdered molecular sieves and photolyzed 8 min with 300 and 350 nm light. The solution was filtered, concentrated, and chromatographed with 2:8 EtOAc/hexane containing 1% Et₃N to give the bis(TEMPO) adduct 3-**15** (3 mg, 0.007 mmol, 7%). ¹H NMR (400 MHz, CDCl₃) δ 0.45 (s, 3), 0.62 (s, 3), 0.75 (s, 3), 0.85 (s, 3), 1.03 (s, 3), 1.05 (s, 3), 1.06 (s, 3), 1.14 (s, 3), 1.2–1.7 (m, 12), 5.32 (s, 1), 7.30 (m, 1), 7.84 (d, 1), 8.56 (d, 1), 8.70 (2, 1). ¹³C NMR (100 MHz, CDCl₃) 16.9, 17.0, 20.16, 20.23, 20.6, 20.8, 29.7, 31.1, 32.0, 33.3, 34.4, 39.5, 40.3, 60.5, 85.4, 123.5, 127.3, 129.7, 134.8, 149.5. IR (CDCl₃) 1780 cm⁻¹. EIMS *m/z* 276, 247, 182, 156, 140, 119, 91, 83, 69, 55.

Reaction of 4-Pyridylketene (4-**15**) with TEMPO

4-Diazoacetylpyridine (21.3 mg, 0.145 mmol)^{5a} and TEMPO (46 mg, 0.30 mmol, 2.1 equiv) in hexane (14 mL) were purged 30 min with argon, and photolyzed 15 min with 300 and 350 nm light. The solution was stirred for 2 h at room temperature. The solution was filtered, concentrated, and chromatographed with EtOAc/hexane, 1:9–3:7 to give the bis(TEMPO) adduct 4-**15** (1.9 mg, 0.018 mmol, 3%). ¹H NMR (400 MHz, CDCl₃) δ 0.4–1.6 (m, 36), 5.26 (s, 1), 7.41 (d, 2, *J* = 6.0 Hz), 8.60 (d, 2, *J* = 6.0 Hz). ¹³C NMR (100 MHz, CDCl₃) 17.1, 17.2, 20.3, 20.4, 20.8, 31.2, 32.1, 33.5, 34.4, 39.4, 39.6, 40.5, 59.9, 60.3, 60.8, 60.9, 86.9, 122.5, 148.0, 150.0, 169.8. IR (CDCl₃) 1776 cm⁻¹. EIMS *m/z* 432, 156, 140, 69. HREIMS *m/z* calcd for C₂₅H₄₂N₃O₃ (MH⁺) 432.3203, found 432.3226.

Kinetic measurements

The kinetics of the reactions of ketenes were measured as reported previously by monitoring the disappearance of ketene in the presence of various concentrations of excess

TEMPO by UV.^{1b–h} Second order rate constants for reaction were obtained from plots of *k*_{obs} versus [TEMPO] as reported in Table 3.

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