Nitroxyl Radical Addition to Pentafulvenones Forming Cyclopentadienyl Radicals: A Test for Cyclopentadienyl Radical Destabilization

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Photochemical Wolff rearrangements in alkane solvents of the 6-diazo-2,4-cyclohexadienones **4** and **13–15** give pentafulvenone (**1**), 2,3-benzopentafulvenone (**2**), dibenzopentafulvenone (**3**), and 2,4-di-*tert*-butylpentafulvenone (**16**), as identified by conventional UV and IR spectroscopy. Reactions of these fulvenyl ketenes with tetramethylpiperidinyloxyl (TEMPO) proceed by addition of TEMPO to the carbonyl carbon forming delocalized radicals for **1** and **2** which add one or more further TEMPO molecules, while the initial radical products formed from **3** and **16** dimerize. The rate constants of these reactions compared to hydration rate constants for the same compounds show the benzannulated derivatives **2** and **3** fit a previous correlation k_2 (TEMPO) vs $k((H_2O)$, whereas for **1** and **16** there is evidence for inhibition of reactions with radicals. The deviations are consistent with an absence of aromatic stabilization of the cyclopentadienyl radicals from **1** and **16** that is compensated in the benzannulated derivatives.

Pentafulvenone $(1)^1$ and its mono- and dibenzo derivatives 2^2 and 3,³ respectively, have been of great recent interest, particularly regarding their reactivity with H₂O. The photochemical generation of substituted derivatives of indenylideneketene (2) formed by Wolff rearrangement of diazo ketones analogous to 4 (eq 1) and the subsequent ketene hydration to the corresponding acids play a pivotal role in the manufacture of integrated circuits by microlithography,⁴ and so the photochemical generation and ionic chemistry of 2 as well as those of 1 and 3 has attracted intensive investigation.¹⁻³ However, the free



radical chemistry of **1**–**3** has been neglected, and indeed, the entire area of the reactivity of ketenes with free radicals has not been the subject of systematic study until our recent investigations.⁵ The radical chemistry of **1**–**3** is also of interest because the 5 π electron cyclopentadienyl radical is intermediate between the 4 π electron antiaromatic cyclopentadienyl cation^{6a–c} and the 6 π electron aromatic central ring of the cyclopentadienyl,

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indenyl, and fluorenyl anions.^{6b,d} The possible stabilization of the fulvenones **1**–**3** due to 6 π electron aromatic character has also been investigated,^{6e} and the question of antiaromaticity in open shell systems has been reviewed.^{6f}

The cyclopentadienyl and indenyl cations are strongly destabilized and are antiaromatic by a number of other criteria, including magnetic susceptibility exaltation and nucleus independent chemical shifts.^{6b} The fluorenyl cation is destabilized by 5-10 kcal/mol relative to the diphenylmethyl (benzhydryl) cation and has been described as nonaromatic as a result of the antiaromatic character of the central cyclopentadienyl ring being partially compensated by the aromaticity of the benzene rings.^{6b}

The first cyclopentadienyl radical to be studied was the long-lived pentaphenylcyclopentadienyl radical reported by Ziegler and Schnell in 1925,^{7a} and others include aryl-substituted derivatives^{7b} as well as pentaisopropyl,^{7c} pentafluoro,^{7d} pentachloro,^{7e} pentamethyl,^{7f-h} and the parent.^{7i-q} The singlet and triplet states of these radicals are usually close in energy. Indenyl⁸ and fluorenyl⁹ radicals have also been investigated.

While these previous investigations have revealed that cyclopentadienyl radicals are quite reactive unless heavily substituted, there has been little explicit consideration of whether these species resemble more closely the highly stabilized aromatic cyclopentadienyl anions^{6b,d} or the highly destabilized antiaromatic cyclopentadienyl cations.^{6b,c} Resonance stabilization energies (RSE)^{8b,9c} of

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 Table 1. Bond Dissociation Enthalpies for H

 Detachment from Hydrocarbons (kcal/mol)



^a Reference 8b. ^b Reference 8d. ^c Reference 10b. ^d Reference 10a.

radicals provide a criterion to evaluate the effects of electron delocalization, and are obtained as the difference of the bond dissociation energies (BDE) of precursors R_sX which form delocalized radicals and the BDE of substrates $R_{ns}X$ which form comparable nondelocalized radicals (eq 2).

$$RSE(R_{s}\bullet) = BDE(R_{ns}X) - BDE(R_{s}X)$$
(2)

The C-H bond dissociation energies of cyclopentadiene (5), indene (6), and fluorene (7) are 81.5 ± 2.7 , $81.1 \pm$ 2.4, and 81.2 \pm 2.4 kcal/mol, respectively (Table 1).8d The BDE of reference substrates 8-11 that do not form cyclic conjugated radical systems are given in Table 1, and these indicate that there is a large gain in RSE when the conjugated system is constrained to near-planarity, as, for example, the 5 kcal/mol difference between Ph2- CH_2 (8) and 9. However, the BDE of cyclopentadiene, indene, and fluorene are consistently above those of the models held close to planarity but not fully conjugated and are the same as for Ph₂CH₂. Thus, these BDE data suggest a destabilizing effect of 5 kcal/mol in the cyclopentadienyl radical and its mono- and dibenzo analogues. This destabilization may arise from unfavorable antiaromatic electronic effects in the 5π electron cyclopentadienvl radical moieties.

Notably, there is a large decrease in the C–H BDE of cyclopentene (82 kcal/mol) compared to cyclopentane (94.8 kcal/mol),^{10a} but incorporation of a second double bond in cyclopentadiene gives a BDE (81.5 kcal/mol) that is essentially unchanged (Table 1). The BDE of cyclopentane is less than that of cyclohexane (99.6 kcal/mol),^{10a} and this parallels the greater ease of forming cyclopentyl

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compared to cyclohexyl carbocations, a phenomenon ascribed to the relief of eclipsing interactions in the cyclopentyl derivatives.^{10c} Such effects would not be present in the cyclic dienes.

In our previous work, calculations of the reaction of CH₂=C=O with H₂NO[•] using B3LYP methods have shown that while addition at C_β is predicted to be endothermic by 6.1 kcal/mol the addition at the carbonyl carbon is exothermic by 18.7 kcal/mol (eq 3).^{5b} Experimentally, we have observed that 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO, TO[•]) reacts with ketenes with a first-order dependence on [TEMPO] forming products derived from initial addition of TEMPO to the carbonyl carbon.^{5d,e} As illustrated for PhCH=C=O, this results in an intermediate radical that may add a second TEMPO at C_β (eq 4), while the fate of other such initial radicals depends on the particular structure involved.^{5b-f}

$$H_{2}NOCH_{2}\dot{C}=O \xrightarrow{\Delta E} = CH_{2}=C=O + H_{2}NO \cdot \frac{\Delta E}{-18.7 \text{ kcal/mol}} CH_{2}=C=O + H_{2}NO \cdot \frac{\Delta E}{-18.7 \text{ kcal/mol}} CH_{2}CO(A)$$
(3)

PHCH=C=O + TO· PhCHCO₂T <u>TO·</u> PhCH(OT)CO₂T (4)

Results and Discussion

The question examined here is whether radical additions to fulvenones 1-3 might provide a route to substituted cyclopentadienyl, indenyl, and fluorenyl radicals. The reactivities of 1-3 might further be utilized to examine any change of aromatic stabilization during the reaction.

Calculations at the B3LYP/6-31G*//B3LYP/6-31G* level were carried out for the structures and energies of **1** and the adduct **12** formed by reaction with aminoxyl (H₂NO[•]) as we have done previously,^{5a,b} and the reaction was found to proceed by attack in the molecular plane at the carbonyl carbon and to be exothermic by 24.6 kcal/mol (eq 5). Thus, this reaction is more favorable than that of CH₂=C=O (eq 3) by 5.9 kcal/mol. As discussed previously,^{5a} this level of theory has been widely utilized for nitroxyl radicals and has been found to give meaningful results.

$$\sum_{\text{C=0}} + H_2 \text{NO} \cdot \frac{\Delta E}{-24.6 \text{ kcal/mol}} \qquad (5)$$

For the generation of the fulvenones 1-3, the strategy of our initial studies^{5d} of the reaction of TEMPO with ketenes formed by Wolff rearrangement was utilized. Thus, we have found that a number of ketenes that had not been previously directly observed in solution at room temperature as long-lived species could be prepared and their IR and NMR spectra measured by conventional means.^{5d,e} This success depended upon the use of low concentrations to facilitate conversion of the diazo ketones and to minimize ketene dimerization and on the use of hydrocarbon solvents with low water content to prevent hydration. For this study, the known diazo ketones **4** and **13–15** were photolyzed in alkane solvents,

Table 2. Spectral Properties of Fulvenones

]	UV (nm)		
fulvenone	obsd	lit.	obsd	lit.
1	2129	2133, ^{<i>a</i>} 2138 ^{<i>b</i>}	260, 266	259, ^c 260 ^d
2	2124, 2108	2117, 2128 ^e	251, 307	250, 310 ^f
3° 16	2126, 2114 2116	2110, ^a 2135, ^b 2121 ^g 2120 ^b	226 261	260 ^h

^{*a*}Reference 1i. ^{*b*} Reference 1e. ^{*c*} Reference 1a. ^{*d*} Reference 1b. ^{*e*} Reference 2j. ^{*f*} Reference 2i. ^{*g*} Reference 3b. ^{*h*} Reference 3c.

and the product solutions gave IR and UV spectra consistent with the formation of fulvenones 1-3 and 16, respectively, and with available literature data, as summarized in Table 2.



The diazo ketone **13** was quite insoluble, and upon photolysis the yellow product **17** (eq 6) was always isolated. This depressed the yields of other products. This material has been identified previously^{1c,d} and evidently arises from reaction of fulvenone **1** with the diazo ketone **13**.



Photolysis of degassed solutions of 13 in the presence of TEMPO and maleic anhydride gave after filtration a 51% recovery by weight of soluble material from which was isolated 17 (33%) and the new products 20 and 21 in 4 and 6% yields, respectively. The structure of 20 was established by 2D NMR techniques, and the structure of **21**, which was the major product in the absence of maleic anhydride, was established by X-ray crystallography.¹¹ The same products were observed when the reaction was conducted by first generating 1 by photolysis of 13 and then adding TEMPO. A working hypothesis for the formation of 20 and 21 is shown in Scheme 1 and is discussed in more detail below. The solutions were degassed prior to reaction, and so mechanisms involving reaction with adventitious O₂ were excluded. Also, while formation of endoperoxides by reaction of cyclopentadienes with ¹O₂ and their cleavage is known,¹² such a reaction with ³O₂ would be unusual. The formation of the product **20** with incorporation of one oxygen atom and two TEMPO moieties is also not supportive of a reaction

⁽¹¹⁾ X-ray crystallographic data for ${\bf 21}$ and ${\bf 31}$ are given in the Supporting Information.

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with O_2 . A product analogous to **20** was also observed in the reaction of indenylketene (**2**) with TEMPO (Scheme 3, vide infra).

The isolated yields of 20 and 21 from 13 are modest,

and this is partly due to the formation of **17** and the difficulties of separating these products. The inhibition of the formation of **21** by maleic anhydride could arise from trapping of the radicals responsible for the transformation of **20** shown in Scheme 1.

Generation of the fulvenone **16** from **15**¹³ followed by the addition of TEMPO led to a product mixture containing the known^{1g} fulvene 23 analogous to 17 and a mixture of two isomeric products 24a,b in a 37/63 ratio (Scheme 2). These were not well separated by preparative chromatography, although a clean resolution was observed by analytical HPLC. The products were, however, positively identified by the NMR spectra of the mixture, including COSY, HMBC, and HSQC experiments. These products were evidently formed by dimerization of the intermediate radical 25, followed by 1,5-hydrogen migrations^{14a-c} in one of the rings leading to **24b** (Scheme 2). Dimerization of the parent cyclopentadienyl radical is known to give 26a, which upon warming gives 26b without observation of a product analogous to 24b in which only one hydrogen has undergone migration.^{70,p}

Photolysis of **4** in hexane to give **2** followed by addition of TEMPO and examination of the product by ¹H NMR revealed formation of an unstable bis-TEMPO adduct **27** as 74% of the product, together with 4% of the isomer **28** and 18% of the indenone **29** (Scheme 3). On standing, **27** underwent gradual thermal conversion to the ketone **29**, while upon chromatographic separation complete conversion of **27** and **28** to **29** was observed.

Photolytic generation of **2** in the presence of TEMPO led to a mixture of **27**, **28**, and **29** in relative yields of 14, 41, and 41%. The enhanced yield of **28** observed under these conditions is suggestive of isomerization of **27** to **28**, and addition of Et₃N to **27** gave efficient conversion to the isomer **28**, which gradually formed **29** upon standing. The conversion of **27** to **29** was also enhanced by the addition of HOAc. The structures of **27–29** were clearly indicated by their characteristic spectral properties, including ¹H and ¹³C NMR, IR, and mass spectra. In particular, the structures of **27** and **28** were confirmed by COSY, HMBC, and HSQC NMR experiments.

Photolysis of **14** to form **3** followed by the addition of TEMPO gave a product containing 50% unreacted **14** by ¹H NMR, and the dimer **31** of the radical **32** (eq 7) was isolated in 32% yield based on the starting **14**. At 25 °C,



the ¹H NMR spectrum of **31** was broadened, but at -20

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Table 3. Rate Constants for Reactions of Fulvenones with TEMPO at 25 $^\circ\text{C}$ in Octane

fulven- one	$\frac{k_2 \text{ (M}}{\text{obsd}}$	$\frac{(1 \text{ s}^{-1} \text{ s}^{-1})}{\text{calcd}^f}$	<i>k</i> (H ₂ O)	$(k_2^{\mathrm{TEMPO}}/k^{\mathrm{H_2O}} imes 10^5)$
1	20.2^{a}	580	$9.0 imes 10^5 \ 1.2 imes 10^6 \ 1.07 imes 10^5 \ 4.9 imes 10^{3e}$	2.2
2	422^{b}	815		35
3	482^{c}	50		450
16	0.120^{d}	1 45		2 4

^{*a*} $k_{obs} = (20.2 \pm 0.9) M^{-1} s^{-1} [TEMPO] + (2.96 \pm 0.47) \times 10^{-3} s^{-1} b k_{obs} = (422 \pm 19) [TEMPO] M^{-1} s^{-1} + (1.05 \pm 0.08) \times 10^{-2} s^{-1} c k_{obs} = (482 \pm 9) [TEMPO] M^{-1} s^{-1} + (1.31 \pm 0.10) \times 10^{-2} s^{-1} d k_{obs} = (0.120 \pm 0.003) [TEMPO] M^{-1} s^{-1} + (7.19 \pm 1.4) \times 10^{-5} s^{-1} e$ This work; average of runs at pH 3.6, 4.6, 6.7 ^{*f*} Calculated from eq 8 using measured $k(H_2O)$ values.

°C a well-resolved spectrum was obtained, showing four CH₃ groups for two nonequivalent TEMPO residues and eight well-resolved aryl protons for two nonequivalent fluorenyl groups. This behavior is in accord with the previous assignment of the dimers of 9-fluorenyl radicals as possessing a gauche conformer with nonequivalent aryl groups,¹⁵ and this was confirmed by an X-ray determination for **31**.¹¹

The kinetics of the reactions of 1-3 and 16 with TEMPO were measured by photolysis of the diazoketones 4 and 13-15 in isooctane solvent, followed by addition of excess TEMPO, and observing the decrease of the UV absorption of the ketene. Thus, even though the yields of isolated products from the ketene reactions with TEMPO were not high, the kinetics of their reactions could still be reliably monitored. Plots of k_{obs} versus [TEMPO] gave linear plots from which second-order rate constants k_2 (Table 3) were derived. Solutions of **1**-**3** and 16 in the absence of TEMPO decayed with first-order kinetics, and the derived rate constants agreed with the rate constants derived from the plots of k_{obs} vs [TEMPO] at [TEMPO] = 0. This decay in the absence of TEMPO is attributed to hydration by adventitious H₂O, as confirmed in a previous example.¹⁶ The hydration rate constant of 16 was also measured (Table 3). Full kinetic data are given in the Supporting Information.

Mechanistic Considerations

The reaction of pentafulvenone (1) is predicted by B3LYP calculations to react with H₂NO[•] in a process (eq 5) that is exothermic by 24.6 kcal/mol, and this is confirmed experimentally by the high reactivity of **1** with TEMPO, which is comparable to the most reactive of a group of ketenes examined previously.^{5d,e} 2,4-Di-tertbutylfulvenone 16 is significantly less reactive than 1 in both the reaction with H₂O and with TEMPO, by factors of 180 and 170, respectively. Several causes may be envisaged for the lower reactivity of 16, including reactant stabilization by the alkyl substituents, and substituent interference with TEMPO attack and with solvation. but the combination of these effects is the same in both reactions, as the rate ratio $k(H_2O)/k_2(TEMPO)$ is essentially constant. The indenylidene and fluorenylidene ketenes 2 and 3 are significantly more reactive toward TEMPO than 1, by factors of 21 and 24, respectively.

Pathways for the formation of the products from 1-3 and 16 are shown in Schemes 1-3 and eq 7, although

the details of these processes have not been proven. As demonstrated^{5a-f} for TEMPO reactions with other ketenes, the reactions of **1**–**3** and **16** proceed by initial attack at the carbonyl carbon, forming the radical intermediates **18**, **30**, **32**, and **25**, respectively. In the cases of **18** and **30**, the intermediate radicals are captured by a second TEMPO radical, whereas **25** and **32** dimerize. Initial adducts **19a** (not observed) from **18** (Scheme 1) and **27** from **30** (Scheme 3) are formed by allylic rearrangement analogous to the formation of PhCH(OT)CH=CHCO₂T from TEMPO and PhCH=CHC=C=O^{5d,e} and are also labile because of the possibility of cleavage of the O–N bonds. Further reactions of the highly substituted radicals **25** (Scheme 2) and **32** (eq 7) with TEMPO are inhibited, and in both cases dimers are formed.

A working hypothesis for further transformation of 19a involves a 1,5-hydrogen shift^{14a-c} forming **19b** (Scheme 1), which by cleavage of a weak N–O bond could form a highly delocalized radical that could add TO[•] to form the observed 20. We have reported an analogous homolytic RO-T bond cleavage,^{5b} and a comparable heterolytic cleavage is implicated in the formation of 29 (Scheme 3). Hydrogen abstraction from 20 by a radical such as T. could form the highly conjugated radical 20a, which could react by ring closure to an oxiranyl radical^{14d,e} with H migration forming 20b. Addition of TO and further migration could form 20c, which leads to the observed 21. Hydrogen migration to radical sites as in the formation of **20b** is known in favorable circumstances, ^{14f,g} and there are precedents for the cyclization by a carbonyl group leading to an oxiranyl radical in a radical dication^{14h} and radical attack on oxiranes with ring opening as in the formation of 20c.14i An alternative but also speculative mechanism involving migration of a carboxy group^{14j} is given in the Supporting Information. Detailed investigation of the mechanism of the formation of 21 is beyond the scope of this study.

Rate Correlation

A qualitative correlation found^{5d} between the rate constants for reaction of ketenes with TEMPO and with H_2O has been extended as shown in eq 8.^{5e,f} For the

$$\log k_2$$
(TEMPO) = 1.15 $\log k(H_2O) - 4.08$, (r = 0.93) (8)

indenyl and fluorenyl ketenes **2** and **3**, the ratios of the rate constants predicted by this equation and those observed for reaction with TEMPO are $k_2(\text{pred})/k_2(\text{obs})$ of 1.9 and 0.10, respectively (Figure 1). For the cyclopentadienyl derivatives **1** and **16**, these rate constant ratios are 29 and 12, respectively, indicating significantly slower rates for **1** and **16** with TEMPO than predicted by the correlation.

The reactivities of the ketenes may also be compared by the k_2 (TEMPO)/k(H₂O) rate ratios, which are 35 and 450 for the indenyl and fluorenyl ketenes **2** and **3** and 2.2 and 2.4 for **1** and **16**. This comparison is also suggestive of rate retardations of the reactions of **1** and **16** with TEMPO, which are attenuated in the benzannulated derivatives **2** and **3**.

The rate retardations of the pentafulvenones **1** and **16** with TEMPO are relevant to the question of the possible destabilization of the radical species formed in these

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Figure 1. Plot of log k(TEMPO) vs log $k_{H_{2O}}$ for ketenes (dark circles not included in correlation).

reactions due to the presence of 5π electron antiaromatic effects. These effects echo in greatly diminished form the well-documented destabilization of the cyclopentadienyl, indenyl, and fluorenyl cations, which decreases progressively through this series.^{6b} The relatively high C-H BDE of cyclopentadiene relative to the cyclohexadienyl analogues (Table 1) is also suggestive of such an effect, with an energetic penalty of as much as 5 kcal/mol. The C-H BDE of indene and fluorene are the same as for cyclopentadiene (Table 1), but the analogous ketenes fit the correlation. The pentafulvenones 1 and 16 are significantly less reactive toward TEMPO than are the indenyl and fluorenyl derivatives 2 and 3, and so the diminished k_2 (TEMPO)/k(H₂O) rate ratios for **1** and **16** are not due to their having enhanced reactivity toward H₂O. The high reactivity of 2 and 3 with TEMPO may mask any residual destabilization indicated by the BDE values.

Further insight into the possible antiaromatic character of the cyclopentadienyl radicals is provided by the magnetic properties, which have been studied computationally.⁷ The nucleus-independent chemical shift (NICS), which is a shift calculated for the ring center, is 2.6 for C_5H_5 , compared to the values of 27.6 for the cyclobutadiene singlet (antiaromatic) and -5.3 for the triplet (aromatic), and 49.2 for cyclopentadienyl cation singlet (antiaromatic) and -4.5 for the triplet (aromatic). Benzene has a NICS value of -9.7, and negative values are diagnostic for aromatic species. By this criterion, the triplet cyclopentadienyl radical with a positive NICS of low magnitude is nonaromatic, or modestly antiaromatic. This is consistent with the experimental result that this radical has neither strong aromatic stabilization nor antiaromatic destabilization.

In summary, the question of the possible antiaromatic destabilization of odd-electron cyclic π -systems such as the cyclopentadienyl radical has been raised in a number of different contexts.^{6f} Some evidence for the importance of such effects has been put forward, particularly for the cyclopropenyl and cycloheptatrienyl radicals.^{6f} The cyclopentadienyl radical lies between the highly stabilized anion and the highly destabilized cation and is expected to have properties between these extremes. The bond

dissociation data provides some evidence for modest antiaromatic destabilization, and the kinetic examination presented here suggests a lack of aromatic stabilization. The NICS data^{7q} point to the same conclusion. This extension of the recently developed^{5a-f} reactivity of ketenes with aminoxyl radicals to the fulvenones reveals the novel chemistry of the resulting cyclopentadienyl radicals, and the reactivity of the fulvenones also provides a kinetic method for the evaluation of the stability of cyclopentadienyl radicals. Aromaticity and antiaromaticity are challenging subjects, and the current work illustrates that the fascinating reactivity of the fulvenones with aminoxyl radicals contributes to the elucidation of these effects in cyclopentadienyl radicals.

Experimental and Methods

Calculations at the B3LYP/6-31G*//B3LYP/6-31G* level were carried out using Gaussian 94,¹⁷ and details are provided in the Supporting Information.

Chromatography was performed using silica gel. Solutions for photolysis and kinetic measurement were purged with a stream of argon for 30 min before use. TEMPO was sublimed before use.

Pentafulvenone (1). A solution of diazoketone **13**¹ (3.82 $\times 10^{-5}$ M in isooctane) was irradiated for 2 min with 300 and 350 nm light. The UV spectrum showed essentially complete disappearance of the absorption band of **13** at 408 nm and the formation of new maxima at 260 and 266 nm ($\epsilon 1.1 \times 10^4$ assuming completed conversion to **1**). Absorption due to **17** at 310 and 322 nm was also observed. The identification of **1** was confirmed by the IR absorption of 2129 cm⁻¹ in isooctane.

Reaction of 1 with TEMPO. A solution of 13¹ (12 mg, 0.10 mmol) and TEMPO (79 mg, 0.51 mmol) in 50 mL of hexane was photolyzed with 300 and 350 nm light for 10 min. A brown precipitate formed that was filtered off, and the solvent was evaporated, giving 47 mg of crude product (51% recovery by weight). Chromatography (9/1 hexane/EtOAc) of the product from four such reactions gave in the early fractions fulvene 17 (12 mg, 0.067 mmol, 33%).^{1c,d} Further chromatography gave 8.5 mg of 21, which was rechromatographed to give 21 as an orange solid (3.6 mg, 6%): mp 134 °C dec; ¹H NMR (CDCl₃) δ 1.0-1.8 (m, 36, 2 TO), 2.66 (d, 1, J = 18.3 Hz, trans CHH to CO_2T), 3.06 (d, 1, J = 18.3 Hz, cis CHH to CO_2T), 3.83 (s, 1, OH), 6.55 (s, 1); ¹³C NMR (CDCl₃) & 16.7, 16.8, 20.2, 20.3, 20.4, 20.6, 31.6, 31.9, 32.6, 33.2, 39.1, 39.2, 39.6, 39.7, 47.3, 60.8, 61.4, 74.1, 129.6, 160.9, 174.8, 196.9; assignments confirmed by COSY, HSQC, and HMBC; IR (CDCl₃) 3514, 1751, 1728, 1632 cm⁻¹; UV_{max}(hexane) 248 nm, log ϵ = 3.3; EIMS *m*/*z* 437 (1, MH⁺), 157 (55), 140 (100); HREIMS m/z calcd for C24H41N2O5 437.3015, found 437.3006. A crystal for X-ray study was obtained by slow evaporation of a solution in pentane with ether at 25 °C. In a similar experiment, 13 (12 mg, 0.10 mmol), and TEMPO (80 mg, 0.51 mmol), and maleic anhydride (12 mg, 0.12 mmol) in $5\bar{0}$ mL of hexane were photolyzed as before, and chromatography (4/1 hexane/EtOAc) of the product from 2 such reactions gave 20 as a yellow oil (4 mg, 0.010 mmol, 4%): ¹H NMR (CDCl₃) δ 1.0–1.8 (m, 36, 2 TO), 2.63 (dd, J= 18.3, 3.0 Hz, CHH) 2.95 (dd, J = 18.4, 6.5 Hz, CHH), 5.14 (ddd, J = 6.5, 2.9, 2.3 Hz, CHOT), 8.46 (d, 1, J = 2.2 Hz, C=CH); ¹³C NMR (CDCl₃) δ 16.8, 17.0, 20.0, 20.1, 20.6, 31.8, 31.9, 33.9, 34.0, 38.9, 39.8, 39.9, 44.0, 59.6, 60.2, 60.3, 60.4, 80.5, 137.1, 162.2, 167.7, 198.5; assignments were confirmed by ROESY, COSY, HSQC, and CIGAR, EIMS m/z 421 (MH⁺, 0.3) 264 (6), 156 (75), 140 (15); IR (CDCl₃) 1766, 1730, 1623 cm⁻¹; HREIMS calcd for C24H41N2O4 421.3082, found 421.3066.

Kinetics of the Reaction of 1 with TEMPO. To 1 mL of a solution of 1 in isooctane generated by photolysis in the UV cell of a 4.6×10^{-6} M solution of 13 was added 10 μ L of TEMPO in isooctane. The change in absorption at 260 nm was monitored, and isosbestic points were observed at 234 and 271 nm.

Benzopentafulvenone (2). Photolysis of a 6×10^{-4} M solution of diazoketone 4^{2b} in isooctane with 350 nm light for 1 min in an IR cell led to partial disappearance of the IR bands

due to **4** and the appearance of new absorptions at 2108 and 2124 cm⁻¹ attributed to **2** (lit.^{2j} 2117, 2128 cm⁻¹; lit.^{2d} 2149 cm⁻¹, 12 K). Similar photolysis for 40 s of a 6 × 10⁻⁵ M solution of **4** in isooctane led to the disappearance of the UV band of **4** at 395 nm and the formation of new bands due to **2** at 251 nm ($\epsilon = 2.2 \times 10^4$) and 307 nm ($\epsilon = 5.6 \times 10^3$) assuming complete conversion (lit.²ⁱ 250 nm, $\epsilon = 1.6 \times 10^4$ and 310 nm, $\epsilon = 5.4 \times 10^3$).

Reaction of 2 with TEMPO. A solution of **4** (52 mg, 0.31 mmol) in 30 mL of hexane and TEMPO (99 mg, 0.64 mmol) was irradiated for 18 min with 300 and 350 nm lamps. The solvent was evaporated, and ¹H NMR analysis indicated the presence of **4**, **27**, **28**, and **29** in relative yields of 4, 14, 41, and 41%, respectively. Chromatography (1/1 hexane/ether) gave indenone **29** (81 mg, 0.26 mmol, 85%), which was recrystallized from pentane/ether to give orange needles, mp 92–93 °C. **29**: ¹H NMR (CDCl₃) δ 1.14 (s, 6, 2 CH₃), 1.25 (s, 6, 2 CH₃), 1.58–1.83 (m, 6, 3 CH₂), 6.48 (s, 1, C=CH), 7.31–7.79 (m, 4, aryl); ¹³C NMR (CDCl₃) δ 13.8, 17.7, 28.8, 360, 57.4, 120.3, 120.5, 126.6, 127.2, 127.3, 131.3, 139.0, 145.6, 160.2, 193.7; IR (CDCl₃) 1744, 1716, 1604 cm⁻¹; EIMS *mlz* 313 (M⁺, 0.7), 298 (16), 156 (100); HREIMS *mlz* calcd for C₁₉H₂₃NO₃ 313.1678, found 313.1685.

A solution of 4 (11 mg, 0.064 mmol) in 50 mL of hexane was irradiated with 350 nm light with stirring for 3 min to form 2, and then TEMPO (20 mg, 0.13 mmol) in 50 μ L hexane was added and the solvent was evaporated at 15 °C. Analysis by ¹H NMR revealed the presence of 4, 27, 28, and 29 in relative yields of 4, 74, 4, and 18%, respectively. Spectra of 27 were obtained from this and similar mixtures: ¹H NMR (CDCl₃) & 1.03 (s, 3, CH₃), 1.10 (s, 3, CH₃), 1.13 (s, 3, CH₃), 1.17 (s, 3, CH₃), 1.23 (s, 3, CH₃), 1.26 (s, 3, CH₃), 1.33 (s, 3, CH₃), 1.46 (s, 3, CH₃), 1.5-1.8 (m, 12, 6 CH₂), 5.51 (s, 1, CHO), 7.20-7.40 (m, 2, aryl), 7.60-7.63 (m, 2, 1 aryl H and 1 vinyl H), 7.96 (d, 1, J = 7 Hz, aryl H); ¹³C NMR (CDCl₃) 17.5, 17.6, 20.6, 20.9, 21.2, 21.4, 32.4, 32.44, 34.5, 34.6, 39.5, 40.6, 59.9, 60.7, 61.8, 87.2, 123.1, 124.4, 126.8, 129.1, 133.2, 139.4, 143.3, 146.7, 164.3; the ¹H and ¹³C signals of the carboxy indene moiety were assigned by COSY, HMBC, and HSQC NMR experiments as those from δ 87.2 and lower field; CIMS m/z455 (0.2, MH⁺), 439, 411, 157 (54), 142 (100); HREIMS calcd for C₂₈H₄₂N₂O₃ m/z 454.3195, found 454.3190. Addition of 1.4 μ L of HOAc led to complete conversion of **27** to **29** on standing overnight at 5 °C. Addition of Et₃N (2 μ L, 0.014 mmol) to a similar mixture led to almost complete isomerization to 28: ¹H NMR (CDCl₃) δ 0.90, 0.92, 1.01, 1.02, 1.06, 1.09, 1.26 1.28, 1.2-1.8 (m), 4.36 (s, 1, CHCO), 5.70 (s, 1, C=C), 7.15-7.70 (m, 4, aryl), plus Et₃N peaks; 13 C NMR (CDCl₃) δ 17.6, 17.8, 20.9, 21.0, 21.1, 21.2, 32.4, 32.6, 33.4, 33.9, 39.7, 39.8, 40.4 (2), 51.4, 60.7, 60.8, 61.1, 61.2, 101.5, 118.9, 125.0, 126.6, 127.9, 139.3, 141.0, 162.3, 172.2. Using COSY and HSQC, the carbons of the indenyl carboxy moiety were assigned as those at δ 51.4 and 101.5.

Kinetics of the Reaction of 2 with TEMPO. For each run, 0.5 mL of a stock solution of 1.42×10^{-4} M 2 in isooctane in a 1 mL UV cell was photolyzed for 40 s with 350 nm light to form 2. Then 20 μ L of this solution was injected into 2 mL of a TEMPO solution in isooctane in a UV cell, the change in the UV absorption was monitored at 250 nm, and isosbestic points were observed at 206 and 234 nm. The plot of k_{obs} versus [TO⁻] gave a nonzero intercept attributed to reaction of 2 with traces of moisture, as has been confirmed in another example.¹⁶

Reaction of Dibenzopentafulvenone 3 with TEMPO. A solution of **14** (8 mg, 0.038 mmol) in 50 mL of hexane was photolzyed 100 s with 350 nm light, and TEMPO (6 mg, 0.038 mmol) in 0.03 mL hexane was added, giving an intense yellow color that faded with time. The solvent was evaporated, and the ¹H NMR spectrum showed the presence of unreacted 14 and the product 31 in a 50/50 ratio. Chromatography (15/85 EtOAc/hexane) gave 31 (4 mg, 0.006 mmol, 32%): ¹H NMR $(CD_2Cl_2, -20 \ ^{\circ}C) \delta 0.26, 0.52, 0.58, 1.06 \text{ (each s, 3, CH}_3), 1.2-$ 1.6 (m, 6, CH₂), 5.99 (d, 1, J = 7.8 Hz), 6.62 (t, 1, J = 7.6, 7.3 Hz), 7.03 (t, 1, J = 7.3 Hz), 7.32 (d, 1, J = 7.3 Hz), 7.41, (t, 1, J = 7.3 Hz), 7.49 (t, 1, J = 7.3 Hz), 7.61 (d, 1, J = 7.3 Hz), 8.39 (d, 1, J = 7.8 Hz); ¹³C NMR (CD₂Cl₂, -22 °C) δ 16.9 (CH₂), 19.7 (CH₃) 20.1 (CH₃), 31.3 (CH₃), 31.6 (CH₃), 39.2 (CH₂), 39.5 (CH₂), 60.4, 60.8. 65.5, 118.7, 119.5, 125.7, 126.0, 126.7, 128.1, 128.9, 130.3, 141.3, 141.8, 142.6, 143.8, 171.8; IR (CDCl₃) 1756 cm⁻¹; UV λ_{max} (hexane) 211 (ϵ 7.3 \times 10⁴), 270 (ϵ 2.7 \times 10⁴), 304 (ϵ 4000); EIMS m/z 697 (0.2), 382 (14), 192 (15), 164 (17), 140 (100); HREIMS *m*/*z* calcd for C₄₆H₅₃N₂O₄ (MH⁺) 697.4005, found 697.4015. A crystal was used for X-ray analysis.¹¹

Reaction of Di-tert-butylfulvenone 16 with TEMPO. A solution of 15 (9 mg, 0.040 mmol) in 50 mL of hexane was photolyzed with 300 and 350 nm light for 6 min, a solution of TEMPO (26 mg, 0.17 mmol) in 0.04 mL hexane was added, and the solution stirred overnight. The solvent was evaporated, and ¹H NMR examination revealed the presence of the fulvene 23 and a mixture of the dimers 24a and 24b. The product was combined with another prepared from **15** (11 mg, 0.046 mmol) and TEMPO (0.037 g, 0.24 mmol) and chromatographed with CH₂Cl₂ to give 23 and a 37/63 mixture of 24a and 24b which by HPLC (Porasil column, 99/1 hexanes/EtOAc) showed wellresolved peaks at 9 and 10 min for **24b** and **24a**, respectively. These were not isolated separately but were identified by their spectral data. 24a: ¹H NMR (CDCl₃) δ 0.8–1.8 (m, CH₃ and CH₂), 1.16 (s, 9, t-Bu), 1.25 (s, 9, t-Bu), 4.26 (d, 2, J = 1.3 Hz, CH), 6.22 (d, 2, 1.5 Hz); ¹³C NMR (CDCl₃) δ 63.0, 129.4, 131.4, 152.2, 153.7, 170.2. **24b**: ¹H NMR (CDCl₃) δ 1.17, 1.21, 1.23, 1.29 (each s, 9, t-Bu), 2.88 (d, 1, J = 23.4 Hz, CHH), 3.04 (d, 1, J = 23.6 Hz, CHH), 4.48 (d, 1, J = 1.6 Hz, CH), 6.20 (d, J = 1.6 Hz); $^{13}\mathrm{C}$ NMR (CDCl₃) δ 44.3, 62.5, 129.7, 130.9, 132.6, 148.0, 149.4, 150.6, 154.4, 158.3, 167.4, 170.4; these peaks were assigned by DEPT, COSY, HSQC, and HMBC, and others were at δ 16.6, 16.8, 20.7, 21.5, 30 0, 30.9, 31.0, 31.2, 32.0, 32.3, 33.3, 34.0, 34.1, 34.2, 34.3, 34.5, 35.6, 39.2, 40.6, 59.9, 60.0, 60.3; IR (CDCl₃) 1759, 1727 cm⁻¹; UV λ_{max} (pentane) 273 nm $(\epsilon = 9900)$

Kinetics of Reactions of 3 and 16 with TEMPO. A 1.9 $\times 10^{-3}$ M solution of **14** was irradiated for 1 min with 350 nm light to form **3**, 10 μ L of this solution was injected into a solution of TEMPO in isooctane ((3.76–17.6) $\times 10^{-5}$ M), and the decrease in the absorption of **3** at 226 nm was observed. Isosbestic points at 213, 248, and 257 nm were noted. The second-order rate constant was obtained as the slope of a plot of k_{obs} vs [TEMPO]. A nonzero intercept due to reaction of **3** with H₂O was observed, and this was confirmed by measuring the rate constant for reaction of **3** in isooctane without TEMPO and by observing the UV spectrum for the resulting acid from this reaction.

For the reaction of **16**, 1.0 mL of a 2.6×10^{-4} M solution of **15** was irradiated for 4 min with 300 and 350 nm light, and the resulting solution of **16** was concentrated to 0.08 mL. A 20 μ L portion of this solution was injected into 2 mL of a solution of TEMPO in isooctane, and the decrease in the absorption of **16** at 270 nm or the increase at 310 nm was monitored. Isosbestic points at 230 and 281 nm were noted. Good first-order plots were observed.

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Supporting Information Available: Experimental and computational details, NMR spectra, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.