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Approach to 3-Aminoindolin-2-ones via Oxime Ether Functionalized Carbamoylcyclohexadienes

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O-Benzyloxime ether substituted amidocyclohexadienes were prepared in three steps in good yields from 2-aminoacetophenone. EPR spectroscopic observations and product analyses showed that peroxide-induced decompositions of model compounds led to indolin-2-ones with benzyloxyaminyl substitution at their 3-positions. The cyclization steps were very rapid and took place regioselectively at the C-atoms of the C=N bonds, by 5-*exo* ring closures. An *O*-trityloxime ether analogue was also prepared. The cyclohexadienyl intermediate smoothly yielded an alkoxylaminyl radical again by rapid 5-*exo*-cyclization. However, ring closure was quickly followed by another β-scission step that released the persistent trityl radical and a 3-nitrosoindolin-2-one derivative. EPR spectroscopic evidence showed that the nitroso compound trapped other transient intermediates to afford a series of nitroxides. GC−MS analyses of products formed in reactions including methyl thioglycolate indicated that 1-benzyl-3-methyl-1,3-dihydro-2*H*-indol-2-one was derived from the indolinone moiety.

Introduction

Organotin radical methodology, with its proven reliability and flexibility, is an invaluable preparative tool, but its usefulness is somewhat impaired by neurotoxicity problems. Despite determined efforts over the past few years,[1a−c] the signs are that a single reagent, capable of comprehensively replacing toxic organotin hydrides in radical-mediated processes, is unlikely to be found. Instead, diverse suites of precursors encompassing metal-based,[2a−f] all-organic[1,3a−e] and polymer-bound types,[4a,b] adapted to fulfill targeted chemical roles, are being developed. Functionalized cyclohexadienes combine within one compound the ability to release a desired radical and hydrogen donor capability. We have successfully used them in radical chain reactions,[5a−e] and Studer et al. have introduced silylated 1,4-cyclohexadienes that efficiently release silyl radicals for use in conjunction with an organic halide precursor.[6a,b] 1-Carbamoyl-2,5-cyclohexadienes release carbamoyl radicals (aminoacyl radicals), suitably unsaturated examples of which ring close to afford β- or γ-lactams in moderate yields.[7a−c]

The oxime ether functional group can exhibit up to 3 orders of magnitude higher radical cyclization rates than analogous alkene acceptors.[8] Moreover, a useful functional group remains available for further synthetic elaboration. Other attractive features of oxime ethers are their stability to hydrolysis and the specificity of radical attack at the carbon of the C=N bond. This high regioselectivity was incisively demonstrated by Warkentin's competition studies between 5-*exo* and 6-*endo* alkyl radical ring closures. It was found that even the normally disfavored 6-*endo* attack was preferred at the carbon center over 5-*exo* cyclization at the nitrogen.[9] Currently, radical addition onto oxime ether derivatives is rapidly developing and is becoming a reliable synthetic strategy which can efficiently be applied in syntheses of complex natural products,[10a−c] e.g., 1-deoxynorjirimycin,[11] (+)-7-deoxypancratistatin,[12] morphine alkaloids,[13] (−)-balanol fragments,[14] and pyrrolidine nucleoside analogues.[15]

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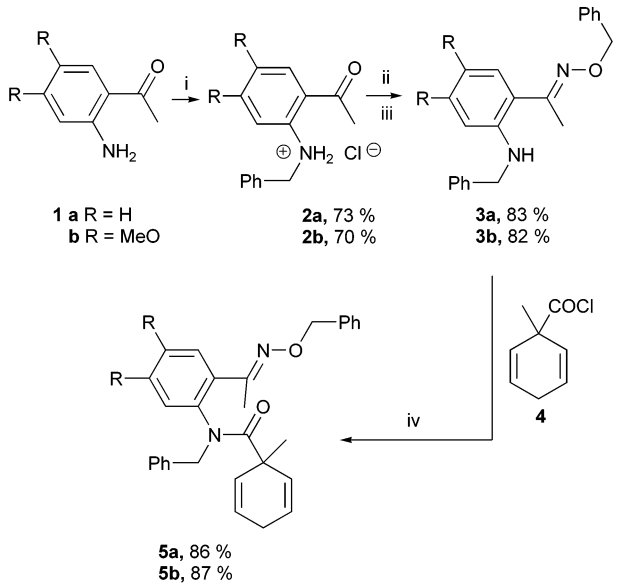
The indole nucleus is a key structural feature in a large number of alkaloids and related compounds, many of which exhibit potent pharmacological activity. This has stimulated interest in finding mild, free-radical-based methods of making the basic nucleus as well as natural products derived from it. For example, Zard has applied xanthates as radical precursors in a synthesis of the sleep regulatory hormone melatonin.[16] Peduncularine was made via cyclization of an amidyl radical derived from an *N*-sulfinyl amide.[17a−c] Indolones were prepared by diethylphosphine oxide mediated cyclizations of iodophenyl amides.[18] We envisaged that our amidocyclohexadienes, suitably functionalized with oxime ether radical acceptors, would be mild, nontoxic carbamoyl radical precursors for preparations of indolones with N-functionality at the 3-position. We prepared several precursors with *O*-benzyl oxime ether acceptors and *O*-trityl oxime ether acceptors and showed by a combination of end product analysis and EPR spectroscopy that this strategy works well.

Results and Discussion

Preparation and Homolytic Reactions of *O*-Benzyl Oxime Ether Substituted Amidocyclohexadienes. We found that alkylation of 2′-aminoacetophenone oxime occurred at the amino rather than the oxime group, and hence, the oxime was not suitable as the starting point. The *N*-benzyl-2′-aminoacetophenone hydrochloride salt **2a** was obtained in good yield and converted to the corresponding *O*-benzyl oxime ether **3a** by treatment with *O*-benzylhydoxylamine in ethanol catalyzed by H_2SO_4 (Scheme 1). We first attempted the preparation of carbamoylcyclohexadiene **5a** using our normal procedure[5e] of slowly adding 1-methylcyclohexa-2,5-diene-1-carbonyl chloride **4** to a mixture of purified amine **3a** and triethylamine in DCM containing a catalytic amount of DMAP. However, no conversion was achieved, and therefore, a pyridine solution of **3a** (containing DMAP) was treated with a DCM solution of **4**, refluxed, and poured into 6 M HCl finally yielding 86% of **5a**. The 4,5-dimethoxy precursor **5b** was prepared in good yield by a similar three-step sequence.

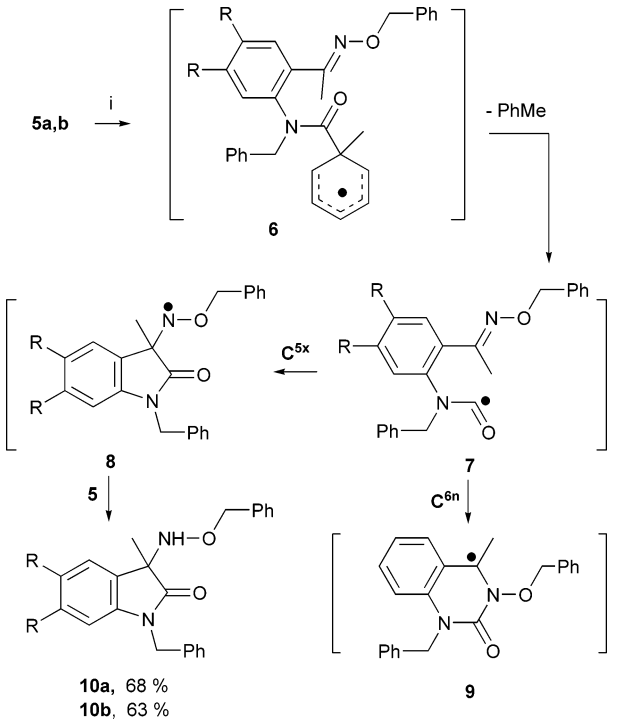
The expected reaction sequence on treatment of **5a** with a peroxide radical initiator is shown in Scheme 2. The bisallylic activation ensures that initial H-abstraction will take place regiospecifically from the cyclohexadiene moiety to generate cyclohexadienyl radical **6**. In refluxing benzene, radical **6** will undergo rapid β-scission to afford carbamoyl radical **7** together with toluene as a benign and easily removed byproduct. 5-*Exo*-ring closure of **7** (**C^{5x}**) should produce the indolinylaminyl radical **8**, which will abstract an H-atom from more **5** and, hence, propagate a chain reaction with 3-substituted indoline-

SCHEME 1. Preparation of *O*-Benzyloxime Ether Substituted Amidocyclohexadienes[a]



[a] Key: (i) $PhCH_2Br$, concd HCl, 60 °C; (ii) $BnONH_2$, EtOH, 12 h; (iii) concd HCl; (iv) pyridine, DMAP, reflux.

SCHEME 2. Preparation of 3-Substituted Indolinones[a]



[a] Key: (i) lauroyl peroxide, RSH, PhH, reflux.

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TABLE 1. EPR Parameters (9 GHz) of Radicals Derived from Carbamoylcyclohexadienes 5 in Neat DTBP

radical	*T*/K	*g*-factor	hfs/G
6a	260	2.0026	*a*(1H) 12.5 *a*(2H) 9.0 *a*(2H) 2.6
6b	255	2.0026	*a*(1H) 12.4 *a*(2H) 9.0 *a*(2H) 2.6
8a	310	2.0047	*a*(N) 13.6 *a*(2H) 2.6
8b	310	2.0044	*a*(N) 13.7 *a*(2H) 2.5

2-one derivative **10** as the end product. Competition from 6-*endo*-cyclization (**C^{6n}**) of carbamoyl radical **7** to generate dihydroquinazolin-2-one intermediate **9** was a potential complication. Literature precedent suggested 5-*exo* mode ring closure, regiospecific for the C-atom of the imine bond, should predominate (see above). However, radical **9** obtained from the 6-*endo* mode would be tertiary benzylic and hence would be strongly thermodynamically stabilized.

To establish which of these reaction channels would prevail we first examined the carbamoylcyclohexadienes using EPR spectroscopy. When **5a** (ca. 5 mg) in di-*tert*-butyl peroxide (DTBP, 0.5 mL) in a quartz tube was degassed and photolyzed with UV light from a 500 W Hg lamp in the resonant cavity of an EPR spectrometer at 230 K a spectrum with EPR parameters appropriate for cyclohexadienyl radical **6a** was obtained (see the Supporting Information and Table 1).

The observed hyperfine splittings (hfs) and *g*-factor were similar to those of related cyclohexadienyl radicals.[7,16] When the temperature of the EPR cavity was increased the spectrum of **6a** weakened and at 310 K it was entirely replaced by a spectrum consisting of a 1:1:1 triplet of triplets. The hfs and *g*-factor (Table 1) were comparable to those of alkoxyaminyl radicals reported in the literature (cf. $PhCH_2N^{\bullet}OCH_2Ph$, $g = 2.0046$, $a(N) = 14.4$ G, $a(OCH_2) = 2.6$ G, $a(CH_2Ph) = 23.8$ G at 210 K)[17] and we attribute this spectrum to the cyclized aminyl radical **8a**. On extinguishing the light, radical **8a** persisted for several minutes, as would be expected because of its appreciable steric shielding. The carbamoyl radical **7a** was not detectable at intermediate temperatures, suggesting that the *5-exo* cyclization was very rapid.

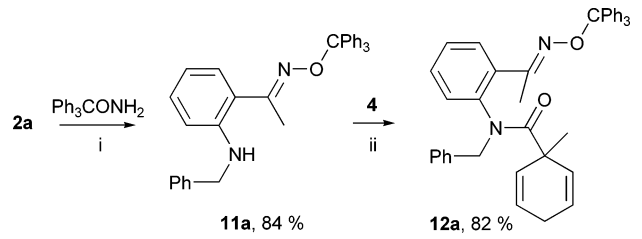
The temperature above which radical **8a** first appeared (ca. 310 K) was similar to the dissociation temperature of other carbamoylcyclohexadienyl radicals,[7b] and hence, the rate constant for release of radical **7** will also be similar, i.e., in the range $10-100\ s^{-1}$ at 300 K. No spectroscopic evidence of the dihydroquinazolin-2-one radical **9a** was obtained at any temperature. However, benzyl type radicals such as **9a** would be difficult to detect because of the large number of weak, narrow lines and therefore the spectroscopic evidence did not conclusively rule out minor *6-endo* cyclization. A very similar set of EPR spectra was obtained from the dimethoxy-compound **5b** and the EPR parameters of radicals **6b** and **8b** are also listed in Table 1.

The spectroscopic evidence indicated that ring closure and indolinone formation took place rapidly. To test the process as a synthetic method we examined the radical induced reaction of **5a** using dibenzoyl peroxide (BPO) in refluxing benzene. However, NMR and GC−MS analyses showed only products from initiator breakdown, even when the reaction was carried out in different solvents and at higher temperatures. We reasoned that addition of a good H-atom donor would enable the ring closed aminyl type radical **8** to be trapped more easily. Accordingly, we carried out a reaction using dilauroyl peroxide as initiator and including a catalytic amount of methyl thioglycolate (RSH). After a 30 h reflux of a benzene solution of **5a**, 1-benzyl-3-[(benzyloxy)amino]-3-methyl-1,3-dihydro-*2H*-indol-2-one (**8a**) was isolated in 68% yield. It is likely that the reaction is subject to polarity reversal catalysis[18] under these conditions. The electrophilic sulfanyl radical RS$^{\bullet}$, derived from methyl thioglycolate, will preferentially abstract hydrogen from the bisallylic site of **5**, due to a favorable polar effect, to produce **6** and regenerate RSH. After ring closure, alkoxyaminyl radical **8** will readily abstract hydrogen from RSH thus leading to formation of **10** and release more RS$^{\bullet}$ to continue the chain. Photolytic radical fragmentation of **5a** was also examined using neat DTBP and UV photolysis for 3 h at 100 °C. GC-MS analysis showed that **10a** was the sole product (apart from initiator derived material). Product isolation was more difficult with this procedure and hence it was less convenient for preparative purposes. None of the dihydroquinazolin-2-one derivative, that would be formed from the *6-endo*-radical **9a**, was isolated or detected by GC−MS from the thermal or photochemical reactions of **5a** or **5b**. It follows that exclusive selectivity for the *5-exo*-closure of the carbamoyl radical onto the C-atom of the C=N bond prevailed. The overall process amounts to a clean route leading from 2′-aminoacetophenones to 1,3-dihydroindol-2-ones in four steps. The products contain nitrogen functionality at C-3 ready for further FG manipulations.

Preparation and Homolytic Reactions of *O*-Trityl Oxime Ether Substituted Amidocyclohexadienes. Clive and Subedi described stannane induced radical ring closures onto *O*-trityl oxime ethers.[19] These cyclizations were followed immediately by β-scission of the O−C oxime ether bond and release of the persistent trityl radical. The advantage of this tactic is that nitroso or oxime functionality is thereby introduced into the *N*-heterocycle, i.e., the process amounts to a partial auto deprotection. To discover if this reaction would work in our tin-free system we made *O*-tritylhydroxylamine by the method of Lutz[20] and reacted it with amino ketone **2a**. The *O*-trityl oxime ether **11a** was obtained in 84% yield by warming an ethanol solution of **2a** and *O*-tritylhydroxylamine to which a drop of H_2SO_4 had been added (Scheme 3). Temperature control was important because at higher temperatures only triphenylmethane and *N*-benzyl-2′-aminoacetophenone oxime were obtained.[21] The desired cyclohexadiene derivative **12a** was prepared in 82% yield on reaction with 1-methylcyclohexa-2,5-diene-1 carbonyl chloride **4** using our standard conditions. Attempts to prepare the 4,5-dimethoxy analogue **11b** were not successful. Reaction of **2b** with *O*-tritylhydroxylamine did not take place at $T < 60$ °C

(19) Clive, D. L. J.; Subedi, R. *Chem. Commun.* **2000**, 237.
(20) Lutz, W. B. *J. Org. Chem.* **1971**, *36*, 3835.
(21) Probably by homolytic dissociation of the O−C bond of **11a** and subsequent H-abstraction by both fragment radicals.

SCHEME 3. Preparation of *O*-Trityloxime Ether Substituted Amidocyclohexadienes[a]



[a] Key: (i) EtOH, cat. H_2SO_4, 60 °C; (ii) pyridine, DMAP, reflux.

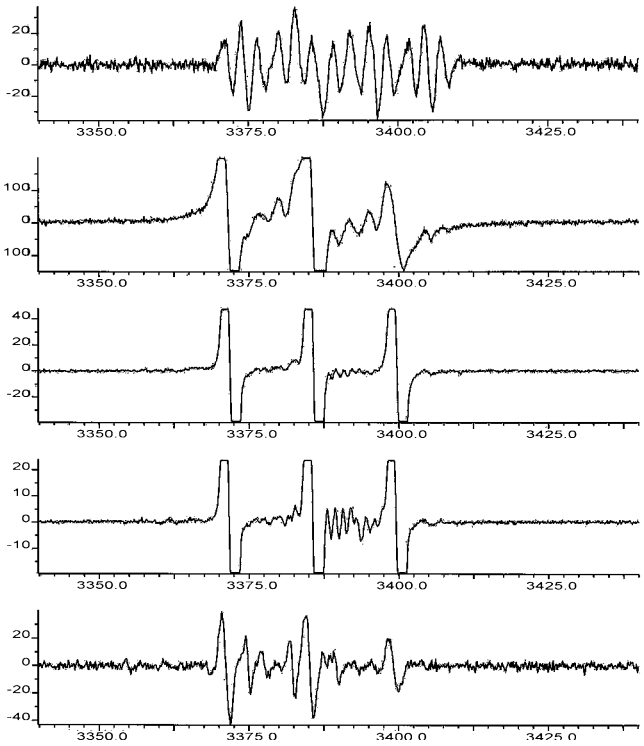


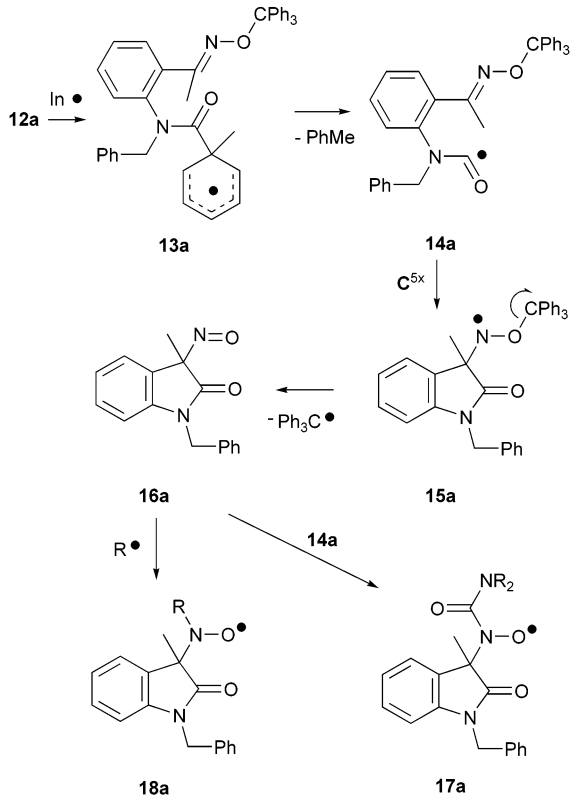
FIGURE 1. EPR spectra obtained on photolysis of **12a** in neat DTBP. Top spectrum at 230 K through 260 K, 320 K, and 330 K to the bottom spectrum at 310 K; after prolonged photolysis.

and at higher temperatures only thermal dissociation products were obtained.

The crystal and molecular structures of amide **12a** were obtained by X-ray diffraction (Supporting Information) and show that the oxime C═N bond of **12a** was formed as the *E*-isomer (trans), unlike most oximes which are generally obtained as *cis*/*trans* mixtures. The C(1)−C(7) bond to the cyclohexadiene was comparatively long (1.555(4) Å) as was the O(14)−C(15) bond of the oxime ether (1.458(3) Å). These bonds undergo homolysis during the course of the reaction so the precursor structure shows they are well adapted for this purpose.

When a degassed solution of **12a** in neat DTBP (1.7 mM) was photolyzed in the resonant cavity of the EPR spectrometer the remarkable sequence of spectra shown in Figure 1 was observed as the temperature was raised. The EPR parameters (g = 2.0026, a(1H) = 12.3 G, a(2H) = 9.1 G, a(2H) = 2.7 G at 230 K) of the radical observed at 230 K (Figure 1, top) show it to be the cyclohexadienyl radical **13a** (Scheme 4). At 260 K a new spectrum consisting of a 1:1:1 triplet (g = 2.0047, a(1N) = 14.0 G)

SCHEME 4. Radicals Generated during Induced Dissociation of 12a

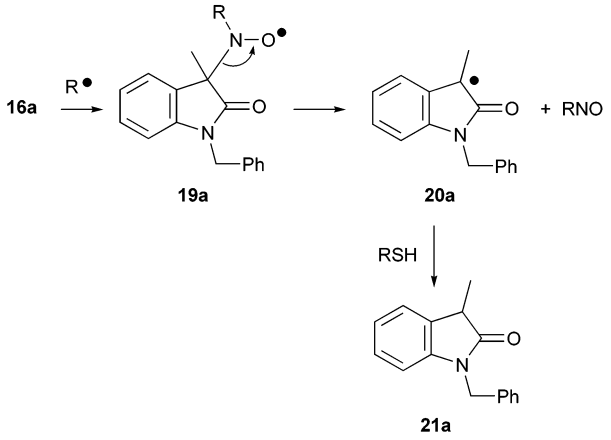


began to appear and had completely replaced that of radical **13a** by 320 K. The EPR parameters indicated this spectrum corresponded to an alkoxyaminyl radical. Loss of toluene from **13a** will produce carbamoyl radical **14a**. However, if **14a** undergoes rapid *5-exo*-cyclization, alkoxyaminyl radical **15a** will be produced. The 1:1:1 triplet is evidently the spectrum of this radical. Species **15a** had a long lifetime (many minutes), as would be expected for radical **15a** which is sterically shielded on both sides of the N-radical center. The 320 K spectrum showed an additional radical, just to high field of the central component of the spectrum from **15a**, and this became much stronger in the 330 K spectrum. Comparison with simulated spectra (see Supporting Information) showed this to be the triphenylmethyl radical [g = 2.0026, a(3H) = 2.7 G, a(6H) = 2.5 G, a(6H) = 1.1 G at 330 K] released by scission of the oxime C−O bond of **15a**.

On prolonged photolysis at the higher temperatures the $Ph_3C^{\bullet}$ radical spectrum weakened and a new spectrum appeared (Figure 1, bottom) with g = 2.0064, a(N) = 7.4 G. These parameters are characteristic of an acyl nitroxide [RC(O)N(O•)R′] that is most likely formed by capture of carbamoyl radical **14a** (which is being continuously formed during the photolysis) by the nitroso compound **16a**, thus producing acyl nitroxide **17a** (Scheme 4). After still further irradiation the spectrum became much more complex due to many overlapping peaks from several nitroxides (**18a**) formed by nitroso-compound **16a** trapping other radicals in the system.

The induced decomposition of **12a** (Scheme 4) will not be a chain reaction because the persistent trityl and alkoxyaminyl radicals (**15a**) (or nitroxides **17a**, **18a**) will

SCHEME 5. Proposed Mechanism for Formation of Indolinone 21a



not readily abstract an H-atom from the precursor cyclohexadiene **12a**. However, by using one equivalent of initiator, we expected to be able to drive the reaction far enough for preparative purposes. Because trityl and radical **15a** are persistent species there was a possibility that the system would be controlled by the persistent radical effect (PRE);[22] i.e., the main products would arise from coupling of **15a** and/or trityl with transient species such as **13a** or **14a**. Attempts to induce reaction of **12a** with BPO in refluxing benzene and in refluxing toluene were not successful. However, addition of a benzene solution of dilauroyl peroxide and methyl thioglycolate over 8 h to a refluxing benzene solution containing **12a**, with continued heating for 24 h, caused essentially complete consumption of the reactant. Attempts to isolate products by chromatography yielded only intractable mixtures. Analysis of the total product mixture by GC−MS showed a range of products including one having $M^+ = 237$, $C_{16}H_{15}NO$, that was probably 1-benzyl-3-methyl-1,3-dihydro-*2H*-indol-2-one (**21a**) accompanied by triphenylmethane, trityl radical dimer and products derived solely from dilauroyl peroxide and methyl thioglycolate.

Similarly, indolinone **21a**, Ph_3CH, and trityl dimer were the main products from a photolytically initiated reaction of **12a** in neat DTBP. However, when the photolysis was carried out with *tert*-butylbenzene as cosolvent GC−MS showed the main product had $M^+ = 266$, $C_{16}H_{14}N_2O_2$ and was probably nitroso compound **16a**, accompanied by Ph_3CH. The intriguing aspect of these results was that product **21a**, formed under thermal conditions, had lost the N-functionality at position 3. Scheme 5 shows a plausible mechanistic rationale of this finding. Nitroso-compound **16a** will very easily trap other radicals to produce tertiary nitroxides **19a**. EPR spectroscopic evidence confirmed this (vide supra). Fragmentation of **19a** by scission of the C−N bond to generate radical **20a**, together with a new nitroso-compound, can readily be envisaged. Radical **20a** is tertiary, benzylic and has an α-carbonyl group so it will be strongly stabilized by resonance delocalization and by steric shielding. These thermodynamic factors probably provide the driving force for this *β*-scission process. Radical **20a** can then pick up an H-atom from RSH or solvent, thus affording the observed product **21a**.

(22) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581.

Conclusions

O-Benzyloxime ether substituted amidocyclohexadienes may be prepared in three steps in good yields from 2-carbonylanilines. EPR spectroscopic observations and product analyses showed that peroxide induced decompositions of model compounds **5a**,**b** led to indolin-2-ones **10a**,**b** with benzyloxyaminyl substitution at their 3-positions. The cyclization steps were very rapid and took place regioselectively at the C-atoms of the C═N bonds, by *5-exo* ring closures. No evidence for even minor *6-endo* ring closure was obtained, even though the resultant dihydroquinazolin-2-one intermediate **9** would be strongly resonance stabilized. This finding showed that carbamoyl radicals selectively reacted at the iminyl C-atom and reinforced previous research that found a strong preference for ring closure of other C-centered radicals onto the C-atoms of oxime ethers.[8,9]

An *O*-trityloxime ether analogue **12a** was also prepared. The cyclohexadienyl intermediate **13a** smoothly yielded alkoxylaminyl radical **15a** again by rapid *5-exo*-cyclization. However, ring closure was quickly followed by another *β*-scission step that released the persistent trityl radical and 3-nitrosoindolinone **16a**. EPR spectroscopic evidence showed that **16a** could trap other transient intermediates to afford a series of nitroxides. Both the trityl and alkoxyaminyl radicals were persistent so the product mixture might have been dominated by their coupling with transient radicals if the process were controlled by the PRE. However, GC−MS analyses of products formed in reactions including methyl thioglycolate, showed a range of products including one derived from the indolinone moiety that had lost the N-functionality at the 3-position. Cross-coupling of transient intermediates with trityl or radical **15a** was not detected. The lack of control by the PRE effect was probably due to the presence of the thiol which donated H-atoms very efficiently. For example, triphenylmethane, as well as trityl radical dimer, were the main products derived from the trityl radical. The complex range of products meant that this method was not useful for preparative purposes. Note however, that the 3-methyl substituent in **16a** blocks tautomerism of the nitroso-compound to the corresponding oxime. For precursors lacking this methyl group the oxime would be the main product so that subsequent trapping reactions, as shown for **16a** in Scheme 4, would not complicate the process.

Experimental Section

EPR Spectra. EPR spectra were obtained with a Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation. Solutions were made up in 4 mm o.d. quartz tubes and deaerated by passing nitrogen for 20 min. Radicals were generated by irradiation, directly in the EPR cavity, with unfiltered light from a 500W super pressure Hg arc. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using the Bruker Simfonia software package. Signals were double integrated using the Bruker WinEPR software and radical concentrations were estimated by reference to a known concentration of DPPH.

(2-Acetylphenyl)benzylammonium Chloride 2a. A mixture of 1-(2-aminophenyl)ethanone **1a** (5 g, 37 mmol) and benzyl bromide (3.16 g, 18.5 mmol) was heated at 50 °C for 3 h to afford a dark yellow crystalline mass. The solid cake was dissolved in hydrochloric acid (36% water solution), reprecipi-

tated into water (300 mL), and filtered. The yellow solid was washed with water and further purified by crystallization using a mixture of ethanol−petroleum ether to yield **2a** as pale yellow crystals (3 g, 73%): mp 72−74 °C; ^{1}H NMR δ 2.61 (3H, s, CH_3), 4.46 (2H, s, CH_2), 6.58−6.66 (2H, m, ArH), 7.25−7.34 (6H, m, ArH) 7.76−7.78 (1H, m, ArH), 9.32 (1H, br s; NH); ^{13}C NMR δ 28.0 (CH_3), 46.7 (CH_2), 112.2, 114.4 (2 × CH), 117.8 (C), 126.9, 127.1, 128.6, 132.6, 135.0 (7 × CH), 138.6 (C), 150.8 (C) 201.0 (C=O); IR (Nujol) ν_{max} 3321 (NH), 1641 (C=O) cm^{-1}. For the corresponding amine: CIMS *m*/*z* 226 $(M + H)^+$, (100); HRMS (CI) calcd for $C_{15}H_{16}NO$ $(M + H)^+$ 226.1231, found 226.1221. Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71, N, 6.22. Found: C, 79.41, H, 6.68. N, 6.16.

1-[2-(Benzylamino)phenyl]ethanone *O*-Benzyloxime 3a. A solution of *O*-benzylhydroxylamine (0.9 g, 7.3 mmol) and **2a** (1.5 g, 5.7 mmol) in ethanol (10 mL) was heated to reflux for 30 min before a drop of sulfuric acid was added. The solution obtained was refluxed overnight before the solvent was evaporated under reduced pressure and the slurry residue made basic with a 6 M NaOH and extracted with DCM (3 × 20 mL). The combined organic layers were dried with $MgSO_4$ and filtered, and the solvent was evaporated to give a yellow oil. Purification was performed by column chromatography (R_f = 0.74) (alumina, eluting with 10% ethyl acetate in hexane) to give a colorless oil. Crystallization in hexane afforded **3a** as a white solid (1.5 g, 79%): mp 52−54 °C; ^{1}H NMR δ 2.33 (3H, s, CH_3), 4.29 (2H, 2 × s, CH_2), 5.01 (2H, s, CH_2), 6.56−6.64 (2H, m, ArH) 7.20−7.38 (12H, m, ArH), 7.95 (1H, br s; NH); ^{13}C NMR δ 13.2 (CH_3), 47.4 (CH_2), 75.9 (CH_2) 111.1 (CH), 115.1 (CH), 117.5 (C), 126.9−129.8, (12 × CH), 138.0 (C), 139.4 (C), 146.8 (C), 157.8 (C=N); IR (Nujol) ν_{max} 3305 (NH), 1603 (C=N) cm^{-1}; CIMS *m*/*z* 331 [$(M + H)^+$, (100)]; HRMS (CI) calcd for $C_{22}H_{23}N_2O$ $(M + 1)^+$ 331.1810, found 331.1802. Anal. Calcd for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.48. Found: C, 79.59; H, 7.11; N, 8.50.

***N*-Benzyl-*N*-[2-[*N*-(benzyloxy)ethanimidoyl]phenyl]-1-methyl-2,5-cyclohexadiene-1-carboxamide 5a.** 1-Methylcyclohexa-2,5-diene-1-carbonyl chloride (0.85 g, 5.4 mmol) was dissolved in dry DCM (5 mL) and added dropwise to a mixture of **3a** (1.2 g, 3.6 mmol) and a catalytic amount of DMAP in dry distilled pyridine (20 mL). The resultant mixture was refluxed overnight before addition of HCl (6 M, 50 mL). The aqueous layer was extracted twice with DCM (2 × 100 mL), and the combined organic layer was washed with water containing a little $NaHCO_3$ (20 mL) and water (20 mL) and dried over $MgSO_4$. The solvent was evaporated at reduced pressure to give a brown oil, which was purified by column chromatography, eluting with 5% ethyl acetate in hexane, to furnish the amide **5a** as a pale yellow oil which crystallized from a mixture ethyl acetate/hexane as colorless crystals (1.4 g, 86%): mp 62−64 °C; ^{1}H NMR δ 1.33 (3H, s, CH_3), 1.92−2.30 (2H, AB, CH_2), 2.19 (3H, s, CH_3), 3.73 and 5.43 (2H, AX, J = 14.3 Hz, CH_2), 4.80−5.67 (4H, m, =CH), 5.24 (2H, s, CH_2), 6.77−7.40 (14H, m, ArH); ^{13}C NMR δ 15.0 (CH_3) 25.7 (CH_2), 29.5 (CH_3), 45.9 (C), 55.0 (CH_2), 76.2 (CH_2), 119.8 (CH), 123.1, 126.8, 127.4, 127.6, 127.9, 127.9, 128.2, 128.7, 128.9, (12 × CH), 129.4, 131.65 131.8 (3 × CH), 134.8 (C), 136.6 (C), 137.8 (C), 139.7 (C), 153.4 (C=N), 174.1 (C=O); IR (Nujol) ν_{max}: 1630 cm^{-1} (C=O); CIMS *m*/*z* 451 ($M^+ + 1$, 25); HRMS (CI) calcd for $C_{30}H_{31}N_2O_2$ $(M + H)^+$ 451.2385, found 451.2401.

Photochemically Initiated Reaction of *N*-Benzyl-*N*-[2-[*N*-(benzyloxy)ethanimidoyl]phenyl]-1-methyl-2,5-cyclohexadiene-1-carboxamide 5a. Amide **5a** (0.05 g) was dissolved in neat DTBP (0.5 mL), the resultant solution was placed in a quartz tube, and the sample was irradiated, at room temperature, with light from a 400 W medium-pressure Hg lamp over a 3 h period. Analysis of the reaction mixture by GC−MS confirmed the presence of the 5-*exo* product 1-benzyl-3-[(benzyloxy)amino]-3-methyl-1,3-dihydro-2*H*-indol-2-one **10a**: peak t_R 34.33 min, *m*/*z* 358 (M^+, 5), 357 (40), 327 (5), 281 (20), 236 (16), 207 (43), 159 (10), 91 (100), together with unreacted amide **5a**. The only detectable impurities were those derived from the photolytic breakdown of DTBP. When a sample containing amide **5a** (0.05 g) in DTBP (0.05 mL) was heated at 100 °C and irradiated for 3 h with UV light GC−MS analysis of the reaction mixture showed only the presence of **10a**, together with byproducts derived from photolytic breakdown of DTBP.

1-Benzyl-3-[(benzyloxy)amino]-3-methyl-1,3-dihydro-2*H*-indol-2-one 10a. Dilauroyl peroxide (0.13 g, 0.33 mmol) was dissolved in benzene (3 mL). The solution was divided into four portions (0.75 mL), and a first portion was refluxed for 10 min before addition of methyl thioglycolate (0.05 mL). The remaining portions were added (1 portion/3 h) to a refluxing benzene solution containing amide **5a** (0.1 g, 0.22 mmol). After complete addition, the solution was refluxed for 30 h and the solvent evaporated at reduced pressure. GC−MS: peak t_R 3.6 min; methyl thioglycolate, peak t_R 10.3 min; undecane (from initiator), peak t_R 16.1 min; disulfide (dimer of thiol), peak t_R 17.1 min; lauric acid (from initiator), peak t_R 23.5 min; docosane (from initiator), peak t_R 28.3 min; 1-benzyl-3-[(benzyloxy)amino]-3-methyl-1,3-dihydro-2*H*-indol-2-one **10a**. The total reaction product was dissolved into DCM (20 mL) and treated with a warm 6 M solution of KOH (50 mL). The aqueous phase was extracted with DCM (3 × 25 mL) and the combined organic layer dried with magnesium sulfate and evaporated at reduced pressure to leave a yellow oil which was purified by column chromatography eluting with a mixture 30% ethyl acetate in hexane (R_f = 0.33) to give a colorless oil which was crystallized from ethyl acetate/hexane to afford **10a** as white crystals (0.07 g, 68%): mp 99−100 °C; ^{1}H NMR δ 1.40 (3H, s, CH_3), 4.36 and 4.48 (2H, AB, J = 10.8 Hz, CH_2), 4.70 and 5.16 (2H, AB, J = 16.0 Hz, CH_2), 6.26 (1H, br s, NH), 6.55−6.89 (2H, m, ArH), 7.03−7.24 (11H, m, ArH)), 7.44−7.46 (1H, m, ArH)); ^{13}C NMR δ 20.2 (CH_3) 41.5 (CH_2), 66.0 (C), 77.7 (CH_2), 109.8 (CH), 123.0 (CH), 124.0 (CH), 127.2, 127.6, 128.0, 128.5, 128.9, 129.0, 129.2, 129.4, (11 × CH), 130.8 (C), 135.6 (C), 137.2 (C), 143.5 (C), 179.1 (C=O); IR (Nujol) ν_{max} 3229 and 3214 (NH), 1718 (C=O) cm^{-1}; EIMS *m*/*z* 358 (M^+, 15), 327 (20), 236 (53), 91 (100), 65 (7); HRMS (EI) calcd for $C_{23}H_{22}N_2O_2$ $(M)^+$ 358.1681, found 358.1674. Anal. Calcd for $C_{23}H_{22}N_2O_2$: C, 77.07; H, 6.19, N, 7.82. Found: C, 77.02, H, 6.02, N, 7.49.

(2-Acetyl-4,5-dimethoxyphenyl)benzylammonium Chloride 2b. A stirred solution of 1-(2-amino-4,5-dimethoxyphenyl)ethanone **1b** (5 g, 26 mmol) and benzyl bromide (2.88 g, 16.8 mmol) in DMF was heated at 60−70 °C for 3 h. The reaction mixture was poured into water (300 mL), acidified with HCl (36%, 10 mL), and stirred overnight. A yellow solid separated from the aqueous phase and was filtered to give a red wine solid which was crystallized from a mixture of ethanol and petroleum ether to yield **2b** as pale yellow crystals (3.8 g, 70%): mp 118−120 °C; ^{1}H NMR δ 2.54 (3H, s, CH_3), 3.74 (3H, s, CH_3), 3.82 (3H, s, CH_3), 4.46 (2H, s, CH_2), 6.08 (1H, s, ArH) 7.17 (1H, s, ArH) 7.26−7.34 (5H, m, ArH), 9.51 (1H, br, s, NH); ^{13}C NMR δ 28.2 (CH_3), 47.5 (CH_2), 55.9 (CH_3), 57.3 (CH_3), 95.2 (CH), 110.4 (C), 115.7(CH), 127.4, 127.6, 129.1 (5 × CH), 139.1 (C), 139.3 (C), 149.1 (C), 156.3 (C), 198.6 (C=O); IR (Nujol) ν_{max} 3293 (NH), 1622 (C=O) cm^{-1}. For the corresponding amine: LRMS (EI) *m*/*z* 285 ($(M + H)^+$, 46), 91 (100); HRMS (EI), calcd for $C_{17}H_{19}NO_3$ (M^+) 285.1365, found 285.1369. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71, N, 4.91. Found: C, 71.45, H, 6.83.N, 4.89.

1-[2-(Benzylamino)-4,5-dimethoxyphenyl]ethanone *O*-benzyloxime 3b. A solution of *O*-benzylhydroxylamine (0.7 g, 5.7 mmol) and **2b** (1.0 g, 3.1 mmol) in ethanol (10 mL) was heated to gentle reflux for 10 minutes before a drop of sulfuric acid was added. The solution obtained was refluxed overnight before the solvent was evaporated under reduced pressure and the residue made basic by a 6M NaOH and extracted with DCM (3 × 20 mL). The combined organic layer was dried with $MgSO_4$, filtered and the solvent eliminated at reduced pressure to give a yellow oil. Purification by column chromatography (R_f = 0.42), (alumina, eluting with 20% ethyl acetate in hexane) and crystallization from a mixture of pentane/ethyl

acetate afforded **3b** as pale yellow crystals (1.0 g, 82%); mp: 82−84 °C, ^{1}H NMR δ 2.31 (3H, s, CH_3), 3.72 (3H, s, CH_3), 3.79 (3H, s, CH_3), 4.26 (2H, s, CH_2), 5.06 (2H, s, CH_2), 6.13 (1H, s, ArH), 6.93 (1H, s, ArH), 7.22−7.28 (10H, m, ArH), 7.91 (1H, br, s, NH); ^{13}C NMR δ 13.7 (CH_3), 48.4 (CH_2), 55.9 (CH_3), 57.8 (CH_3), 76.2 (CH_2), 96.2 (CH), 109.6 (C), 114.6 (CH), 127.4, 127.7, 128.2, 128.6, 128.8, 128.9 (10 × CH), 138.6 (C), 139.7 (C), 140.0 (C), 143.6 (C), 151.5 (C), 157.7 (C═N); IR (Nujol) ν_{max}: 3284 (NH), 1624 (C═N) cm^{-1}; EIMS *m*/*z*, 390 (M)$^+$, (100)], 300 (55), 283 (87), 268 (14), 205 (7), 193 (12), 178 (15), 91 (60), 77 (6). HRMS calcd for $C_{24}H_{26}N_2O_3$ (M^+) 390.1943, found 390.1930. Anal. Calcd for $C_{24}H_{26}N_2O_3$: C, 73.82; H, 6.71, N, 7.17. Found: C, 73.75, H, 6.74, N, 7.14.

***N*-Benzyl-*N*-{2-[*N*-(benzyloxy)ethanimidoyl]-4,5-dimethoxyphenyl}-1-methyl-2,5-cyclohexadiene-1-carboxamide 5b.** 1-Methylcyclohexa-2,5-diene-1-carbonyl chloride (0.5 g, 3.2 mmol) was dissolved in dry dichloromethane (5 mL) and added dropwise to a mixture of **3b** (0.8 g, 2.0 mmol) and a catalytic amount of DMAP in dry distilled pyridine (20 mL). The resultant mixture was refluxed overnight before adding HCl (6M, 50 mL). The aqueous layer was extracted with DCM (2 × 100 mL), the combined organic layer was washed with water containing a little $NaHCO_3$ (20 mL), water (20 mL) and dried over $MgSO_4$. The solvent was evaporated at reduced pressure to give a yellow oil, which was purified by column chromatography, eluting with ethyl acetate in hexane (1:9→3:7) in order to furnish amide **5b** as a pale yellow oil (0.7 g, 87%); ^{1}H NMR δ 1.25 (3H, s, CH_3), 1.95−2.35 (2H, m, CH_2), 2.19 (3H, s, CH_3), 3.47 (3H, s, CH_3), 3.69 and 5.51 (2H, AX, J = 14.0 Hz, CH_2), 3.87 (3H, s, CH_3), 4.84−5.71 (4H, m, CH), 5.23 (2H, s, CH_2), 6.10 (1H, s, ArH), 6.75 (1H, s ArH) 7.09−7.41 (10H, m, ArH)); ^{13}C NMR δ 15.6 (CH_3) 26.1 (CH_2), 30.0 (CH_3), 46.4 (C), 55.2 (CH_2), 55.8 (CH_3), 56.5 (CH_3), 76.6 (CH_2), 111.4 (CH), 115.4 (CH), 119.3 (CH), 123.7 (2 × CH), 127.0 (C), 127.4−129.8, (9 × CH), 132.58 (2 × CH), 133.2 (C), 137.8 (C), 137.9 (C), 147.6 (C), 148.0 (C), 153.8 (C═N), 174.5 (C═O); IR (Nujol) ν_{max}: 1638 (C═O), 1518 (C═C), 1260 (C═C), cm^{-1} CIMS *m*/*z* 511 ((M+H)$^+$, 100); HRMS (CI) calcd for $C_{32}H_{35}N_2O_4$ (M + H)$^+$ 511.2597, found 511.2607. Anal. Calcd for $C_{32}H_{34}N_2O_4$: C, 75.27; H, 6.71, N, 5.49. Found: C, 74.75, H, 6.73, N, 6.35.

1-Benzyl-3-[(benzyloxy)amino]-5,6-dimethoxy-3-methyl-1,3-dihydro-2H-indol-2-one 10b. To a stirred refluxing solution of amide **5b** (0.1 g, 0.25 mmol) in benzene (5 mL) was added 0.5 mL of a solution prepared by dissolving dilauroyl peroxide (0.12 g, 0.3 mmol) in benzene (2.5 mL). After refluxing for 5 min methyl thioglycolate (0.05 mL) was added. The remaining dilauroyl peroxide solution was then added over 8 h. After complete addition, the solution was refluxed for 30 h, the solvent was evaporated at reduced pressure and the product was analyzed by GC-MS; peak t_R 3.6 min; methyl thioglycolate, peak t_R 10.3 min; undecane (from initiator), peak t_R 16.1 min; disulfide (dimer of thiol), peak t_R 17.1 min; lauric acid (from initiator), peak t_R 23.5 min; docosane (from initiator), peak t_R 28.2 min; **10b**. The total reaction product was dissolved in DCM (20 mL) and treated with a warm 6M solution of KOH (50 mL). The aqueous phase was extracted with DCM (3 × 25 mL) and the combined organic layers dried with magnesium sulfate and evaporated at reduced pressure to leave a brown solid which was purified by column chromatography eluting with a mixture 40% ethyl acetate in hexane (R_f = 0.28) to give **10b** as a yellow pale oil (0.05 g, 63%); ^{1}H NMR δ 1.37 (3H, s, CH_3), 3.74 (3H, s, CH_3), 3.84 (3H, s, CH_3), 4.40 and 4.50 (2H, AB, J = 11.0 Hz, CH_2), 4.70 and 5.13 (2H, AB, J = 15.9 Hz, CH_2), 6.26 (1H, s, NH), 6.93−6.99 (1H, m, ArH), 7.10−7.26 (11H, m, ArH), ^{13}C NMR δ 19.9 (CH_3) 43.6 (CH_2), 56.0 (CH_3), 56.5 (CH_3) 65.6 (C), 76.4 (CH_2), 95.3 (CH), 108.1 (CH), 120.8 (C), 126.6, 127.1, 127.4, 127.9, 128.2, 128.4, (10 × CH), 135.2 (C), 136.5 (C), 136.8 (C), 144.9 (C), 149.6 (C) 178.7 (C═O); IR (neat) ν_{max}: 3235 (NH), 1718 (C═O) cm^{-1}; EIMS *m*/*z* 358 (M^+, 15), 327 (20), 236 (53), 91 (100); HRMS (EI) calcd for $C_{25}H_{26}N_2O_4$ 418.1893, found 418.1885.

1-[2-(Benzylamino)phenyl]ethanone *O*-trityloxime 11a. To a stirred solution containing (2-acetyl-phenyl)benzylammonium chloride **2a** (1.0 g, 4.4 mmol) in warm ethanol (10 mL), was added portionwise *O*-tritylhydroxylamine (1.8 g, 6.5 mmol). After complete addition the mixture was heated at 60 °C and stirred for 10 min before adding a drop of sulfuric acid. When a white solid separated from solution, the temperature was lowered to room temperature and the solution stirred for 20 min. The reaction mixture was filtered and the solid cake was extensively washed with ethanol and dried under vacuum, to give white crystals of **11a** (1.8 g 84%); mp: 160−162 °C; ^{1}H NMR δ 2.54 (3H, s, CH_3), 3.93 (2H, 2 × s, CH_2), 6.35 (1H, d, ArH), 6.57 (1H, t, ArH), 6.96−7.01 (1H, m, ArH), 7.17−7.42 (21H, m, ArH)), 7.49 (1H, br s; NH); ^{13}C NMR δ 13.8 (CH_3), 46.5 (CH_2), 91.2 (C−O), 111.1 (CH), 114.7 (CH), 117.8 (C), 126.4, 126.6, 127.1, 127.4, 127.7, 128.2, 128.9, 129.3, 129.7, (22 × CH), 139.7 (C), 143.0 (C), 144.7 (C), 146.7 (C), 157.1 (C═N); IR (Nujol) ν_{max}: 3305 (NH), 1603 (C═N), cm^{-1}; LRMS (ES) *m*/*z* 483 [(M + H)$^+$, (16)], 243 (100), HRMS calcd for $C_{34}H_{31}N_2O$ (M+H)$^+$ 483.2436, found 483.2444. The reaction was also carried out in refluxing ethanol for 10 h, the solvent was evaporated under reduced pressure and the slurry residue made basic by a 6M NaOH and extracted with DCM (3 × 20 mL). The combined organic layers were dried with $MgSO_4$, filtered and the solvent evaporated to give a pale yellow oil. Separation of the products was performed by column chromatography (alumina), eluting with 10% ethyl acetate in hexane to give products deriving from thermal cleavage of **3a**, i.e., *trans*-1-[2-(benzylamino) phenyl] ethanone oxime (major isomer) as pale yellow crystals: mp 52−54 °C; ^{1}H NMR δ 2.33 (3H, s, CH_3), 4.40 (2H, m, CH_2), 6.62−6.70 (2H, m, ArH), 7.12−7.41 (7H, ArH), 7.79 (1H, br s, NH); ^{13}C NMR δ 12.5 (CH_3), 47.5 (CH_2), 111.3 (CH), 115.4 (CH), 117.9 (C), 126.9, 127.1, 128.5, 129.0, 129.9 (CH), 139.4 (C), 146.8 (C), 158.9 (C═N); IR (Nujol) ν_{max} 3337 (NH), 1604 (C═N), cm^{-1}; EIMS *m*/*z* 240 [(M)$^+$, 45), 223(100), HRMS (EI) calcd for $C_{15}H_{16}N_2O$ (M^+) 240.1262, found 240.1269. *cis*-1-[2-(Benzylamino) phenyl]-ethanone oxime as white crystals: ^{1}H NMR δ 2.41 (3H, s, CH_3), 4.21(2H, s, CH_2), 7.05−7.64 (9H, m, ArH), 8.26 (1H, br s, NH); ^{13}C NMR δ 13.9 (CH_3), 47.0 (CH_2), 109.3 (CH), 119.0, 121.9, 122.2, 126.1, 127.8, 128.9 (8 × CH), 135.5 (C), 135.7 (C), 142.5 (C), 151.8 (C═N). Triphenylmethane: ^{13}C NMR δ 56.8 (CH), 126.2, 128.2, 129.4 (15 × CH), 143.8 (3 × C).

***N*-Benzyl-1-methyl-*N*-[2-[*N*-(trityloxy)ethanimidoyl]-phenyl]-2,5-cyclohexadiene-1-carboxamide 12a.** To a stirred mixture containing **11a** (1.4 g, 2.9 mmol) and a catalytic amount of DMAP in dry distilled pyridine (20 mL) was slowly added a solution prepared by dissolving 1-methylcyclohexa-2,5-diene-1-carbonyl chloride (0.67 g, 4.4 mmol) in dry DCM (5 mL). The resultant mixture was refluxed overnight before pouring into aqueous HCl (6 M, 50 mL). The aqueous layer was extracted with DCM (2 × 100 mL), and the combined organic layers were washed with water containing a little $NaHCO_3$ (20 mL) and water (20 mL), and dried over $MgSO_4$. The solvent was evaporated at reduced pressure to leave a reddish oil, which was purified by column chromatography, eluting with ethyl acetate 5% in hexane (R_f = 0.27) in order to furnish **12a** as a white solid which was crystallized from a mixture ethyl acetate/hexane/DCM affording colorless crystals (1.43 g, 82%): mp 164−166 °C; ^{1}H NMR δ_H 1.19 (3H, s, CH_3), 1.85−2.23 (2H, AB, CH_2), 2.42 (3H, s, CH_3), 3.40 and 5.51 (2H, AX, J_{gem} = 14.3 Hz, CH_2), 4.72−5.64 (4H, m, ═CH), 6.53 (1H, d, ArH), 6.78−7.37 (23H, m, ArH); ^{13}C NMR δ 16.4 (CH_3) 25.6 (CH_2), 29.8 (CH_3), 45.8 (C), 54.4 (CH_2), 91.0 (C), 120.1 (CH), 123.1 (2 × CH), 126.8, 127.0, 127.2, 127.6, 127.8, 129.2, 129.6 129.0, (23 × CH), 131.8 (2 × CH), 135.1 (C), 137.5 (C), 138.9 (C), 144.7 (3 × C), 154.4 (C═N), 173.9 (C═O); IR (Nujol) ν_{max} 1632 (C═O), cm^{-1}; ESMS *m*/*z* 625 [(M + Na)$^+$, 100); HRMS (ES) calcd for $C_{42}H_{38}N_2O_2Na$ (M + Na)$^+$ 625.2831, found 625.2823. Anal. Calcd for $C_{42}H_{38}N_2O_2$: C, 83.69; H, 6.35, N, 4.65. Found: C, 83.75, H, 6.49, N, 4.45.

Crystal data for 12a: $C_{42}H_{38}N_2O_2$, $M = 602.74$, colorless plates, crystal size 0.24 × 0.12 × 0.1 mm, triclinic, space group *P*-1, $a = 8.4178(15)$ Å, $b = 12.781(2)$ Å, $c = 16.416(3)$ Å, $\alpha = 84.841(3)°$, $\beta = 83.997(3)°$, $\gamma = 72.819(3)°$, $V = 1674.9(5)$ Å^3, $D_c = 1.195$ Mg/m^3, $T = 125(2)$ K, $R = 0.0647$, R_w 0.0831 for 4539 reflections with $I > 2\sigma(I)$ and 418 variables. Data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation ($\alpha = 0.710\,73$ Å). The structure was solved by direct methods and refined using full-matrix least-squares methods. The structure, atomic coordinates, bond lengths, and coordinates are listed in the Supporting Information.

DTBP-Mediated Photolysis of *N*-Benzyl-1-methyl-*N*-[2-[*N*-(trityloxy)ethanimidoyl]phenyl]-2,5-cyclohexadiene-1-carboxamide 12a. To a solution of amide **12a** (0.03 g) in *tert*-butylbenzene (200 μL) in a quartz tube was added DTBP (50 μL). The tube was capped and irradiated, at room temperature, with light from a 400 W high-pressure Hg lamp for 3 h before the DTBP was evaporated to leave a yellow oil which was analyzed by GC−MS, peak t_R 21.0 min; 1-benzyl-3-methyl-3-nitroso-1,3-dihydro-2*H*-indol-2-one **16a**; *m*/*z* 266 (M^+, 11), 119 (100), 91 (35), peak t_R 22.0 min; triphenylmethane. The only byproducts detected were from photolytic breakdown of DTBP.

Dilauroyl Peroxide Mediated Thermolysis of *N*-Benzyl-1-methyl-*N*-[2-[*N*-(trityloxy)ethanimidoyl]phenyl]-2,5-cyclohexadiene-1-carboxamide 12a. To a refluxing benzene solution (5 mL) containing amide **12a** (0.1 g, 0.16 mmol) was added over 8 h by syringe pump a solution prepared by dissolving dilauroyl peroxide (0.12 g, 0.3 mmol) and methyl thioglycolate (0.05 mL) in benzene (2 mL). After complete addition, the solution was refluxed for 24 h, the solvent was evaporated at reduced pressure to give a mixture which was analyzed by GC−MS. Peak t_R 3.6 min; methyl thioglycolate, peak t_R 10.3 min; undecane (from initiator), peak t_R 16.1 min; disulfide (dimer of thiol), peak t_R 17.1 min; lauric acid (from initiator), peak t_R 23.5 min; docosane (from initiator), peak t_R 21.7 min; triphenylmethane, peak t_R 22.1 min; 1-benzyl-3-methyl-1,3-dihydro-2*H*-indol-2-one **21a**, *m*/*z* 237 (M^+, 100), 208 (35), 146(35), 128 (30), 117(10), 91(100), 77 (12), 65 (10), peak t_R 23.2 min; triphenylmethanol, peak t_R 27.4 min [[4-(diphenylmethylene)-2,5-cyclohexadien-1-yl](diphenyl)methyl]benzene (trityl dimer).

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Supporting Information Available: General experimental methods. EPR spectra of radicals derived from **5a**. Experimental and simulated EPR spectra of the trityl radical and radical **15a**. Experimental details for the preparation of 1-(2-aminophenyl)ethanone oxime, 1-(2-aminophenyl)ethanone *O*-benzyloxime, 1-methyl-2,5-cyclohexadiene-1-carbonyl chloride, *N*-trityloxyphthalimide hydroxyphthalimide, and trityloxyamine. X-ray structure data for compound **12a**. ^{13}C NMR spectra of **5a**, **10b**, and **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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