Photogeneration of Amines from α-Keto Carbamates: Photochemical Studies

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Abstract: We investigate the design of new photoprecursors of organic bases and the steric and electronic factors that control their photocleavage to give free amines. The design strategy involves the protection of an amine with novel [(benzoinyl)oxy]carbonyl groups and substituted analogs. The resulting masked amines owe their photosensitivity to the rich photochemistry of the benzoinyl chromophore. The photochemistry of this chromophore allows for the clean photogeneration of free amine upon irradiation with UV light below 400 nm in both the solid state and in solution. The structure of the benzoinyl chromophore was varied to determine the optimal chromophore design. By varying the chromophore design, the influence of various steric and electronic effects on the photoliberation of free amines from α-keto carbamates could be gauged. Structural modification of the aryl rings was intended to probe the electronic factors of the photocyclization. Substitution at the 2 position was varied to investigate the steric factors involved in photocyclization. The practical potential of these photoactive carbamates as organic sources of photogenerated base was demonstrated spectroscopically (UV, IR, and NMR). GC-MS product studies also proved diagnostic in identifying photogenerated base. The thermal properties of this class of base photogenerators were also determined. α-Keto carbamates derived from 3′,5′-dimethoxybenzoin and its substituted analogs appear particularly attractive. These carbamates undergo near quantitative photocleavage to give free amine along with the corresponding substituted benzo[*b*]furan photocyclization product. Preliminary evaluation of the solid state quantum yield for cyclohexylamine photogeneration from 3,3′,5,5′-tetramethoxybenzoin cyclohexyl carbamate ranged from 0.03 to 0.08 depending on the exposure wavelength. The variation in photoefficiency correlates with the UV absorbance of the keto chromophore indicating direct excitation of the carbonyl group is the preferred pathway for photocleavage.

Introduction

The concept of photochemically labile protecting groups was originally designed to ease complex synthetic schemes.[1] However, in recent years, photodeprotection schemes have found increasing utility in applications demanding the controlled release of reactive species in situ.[2] The impact of such photorelease strategies is particularly diverse and includes caged biomolecule release,[3] combinatorial solid phase peptide synthesis[4] and microlithography.[5]

In microlithography, materials which generate a strong acid upon irradiation led to the development of chemically amplified radiation sensitive imaging materials. The current revolution in organic acid photogeneration has further enhanced the performance of such acid sensitive resist materials.[5] However, the complementary area of base photogeneration has received little attention.[6] Recently, we developed a strategy for base photogeneration by masking amines and diamines as photoactive carbamates.[7−9] Under the action of light, these neutral carbamates decompose to liberate base in a reactive form. The first generation of photoprecursors of organic base is already finding application in a variety of imaging schemes requiring photogenerated base.[10,11] The success of our amine photorelease strategy is further illustrated by the development of a number of base catalyzed chemically amplified resist materials.[12−14]

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Furthermore, the industrial importance of the concept of photogenerated base is illustrated by the large number of patents utilizing base photogeneration in imaging applications.[15]

Of all the common photolabile amino protecting groups, we found the 3,5-dimethoxy-α,α-dimethylbenzyloxycarbonyl (Ddz)[7] and *o*-nitrobenzyloxycarbonyl[8,9] derived photolabile groups to be particularly well suited to the photogeneration of organic base. While base photogenerators derived from these photoprotecting groups have proven useful, they do suffer from some restrictions. For instance, the utility of the *o*-nitrobenzyl class of base photogenerator is limited by the formation of reactive *o*-nitrosocarbonyl compounds, which may undergo deleterious side reactions.[8,9] Overirradiation products such as azo-coupled intermediates act as internal light filters and ultimately restrict the use of these base photogenerators to thin film applications.[12−14] Similarly, severe antibleaching is a significant problem with the 3,5-dimethoxy-α,α-dimethylbenzyloxycarbonyl class of photobase generators.[7]

Problems with the photorelease of organic base in the first generation of materials motivated us to look for new photochemistry that would allow for improved base photogeneration under such demanding circumstances as posed by organic solid state applications. In this regard, we chose to investigate the rich area of photochemistry offered by the desyl chromophore.

We were particularly attracted to a novel photochemical reaction involving photocyclization of a substituted benzoin to form the corresponding inert benzo[*b*]furan.[16,17] In the case of benzoin acetate, 2-phenylbenzo[*b*]furan is isolated as the major isolable product.[16] The formation of the benzo[*b*]furan is accompanied by acetic acid, dihydrobenzoin acetates, and some overirradiation products such as benzofuran photodimer. The efficiency of the photocyclization has been shown to be highly dependent on the nature of substituents on the phenyl rings.[17,18] This is particularly true for the benzyl aromatic ring with meta-methoxy substitution giving the highest yields for photocyclization. This unique photoreactivity has led to the development of the parent benzoinyl chromophore and its substituted analogs as photoremovable protecting groups for a variety of common functional groups. 3′,5′-Dimethoxybenzoin esters have been extensively used as photolabile protecting groups for the carboxyl functionality.[17−19] In these applications, 3′,5′-dimethoxybenzoin acetate was found to liberate the free acid in near quantitative yield with a quantum yield of 0.64 at 365 nm.[17] Benzoinyl and related furoinyl esters have recently been used to mask the carboxyl group during peptide synthesis.[20] Carboxyl protection by the desyl chromophore and its substituted derivatives has been investigated as a method for generating caged neurotransmitters[21] while modification of 3′-methoxybenzoin has been used to prepare a photolabile linker for solid phase synthesis.[22] Derivatization of 3′,5′-dimethoxybenzoin to its carbonate derivative has allowed the protection of a 5′-hydroxyl group in nucleosides[23] as well as a variety of other alcohol and thiol derivatives.[24] The photocyclization of substituted benzoins has also been applied to the caged release of phosphate esters[18,25−28] and inorganic phosphate.[29] In these applications, 3′,5′-dimethoxybenzoin phosphate was found to cyclize with a photoefficiency of 78% which is more than double that of related unsubstituted benzoin phosphates.[26] Furthermore, the photorelease of phosphate from desyl phosphates proceeds at least 1000 times faster and up to 1.24 times as efficiently as *o*-nitrobenzyl derived phosphate esters.[25−27]

As indicated above, desyl photochemistry offers several desirable features which render it particularly attractive for base photogeneration. The literature describing the photochemistry of the desyl chromophore suggests that in comparison with *o*-nitrobenzyl photochemistry, the 3′,5′-dimethoxybenzoin chromophore will exhibit (1) increased stability of photo byproducts; (2) improved photoefficiency, and (3) enhanced rate of photorelease.

This paper describes novel applications of benzoin photochemistry to the preparation of efficient photoprecursors of organic bases: primary and secondary amines. Encouraged by preliminary results from the solution photolysis of cyclohexylamino and piperidino carbamates of 3′,5′-dimethoxybenzoin,[30] we have focused further on the novel photorearrangement of the 3′,5′-dimethoxybenzoin chromophore and its substituted analogs (Scheme 1).[31] A recent independent report on the photogeneration of secondary amines from 3′,5′-dimethoxyben-

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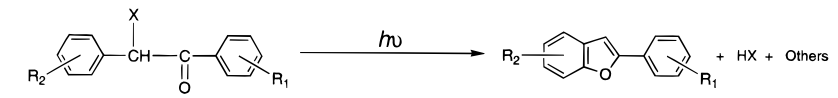
Scheme 1

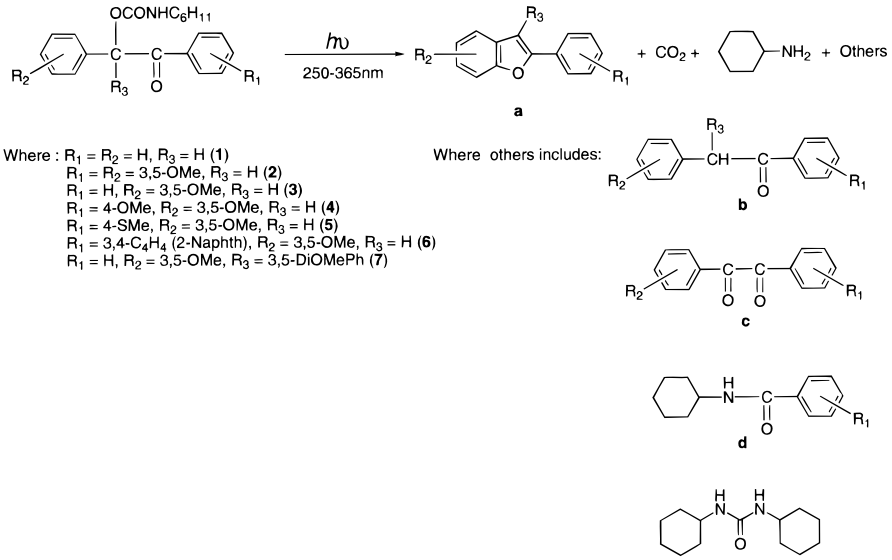


Where X = OAc, $OP(O)(OEt)_2$, $OP(O)O_2^{2-}$, NR_3R_4

R_1, R_2 = H; R_1 = H, R_2 = 3,5-$(OMe)_2$

R_3 = H, R_4 = C_6H_{11}; R_3, R_4 = $-(CH_2)_5-$

Scheme 2



Where : R_1 = R_2 = H, R_3 = H (**1**)
R_1 = R_2 = 3,5-OMe, R_3 = H (**2**)
R_1 = H, R_2 = 3,5-OMe, R_3 = H (**3**)
R_1 = 4-OMe, R_2 = 3,5-OMe, R_3 = H (**4**)
R_1 = 4-SMe, R_2 = 3,5-OMe, R_3 = H (**5**)
R_1 = 3,4-C_4H_4 (2-Naphth), R_2 = 3,5-OMe, R_3 = H (**6**)
R_1 = H, R_2 = 3,5-OMe, R_3 = 3,5-DiOMePh (**7**)

Where others includes:

zoin carbamates has also appeared.[32] Our work focuses on novel applications of benzoin photochemistry in creating new materials for base photogeneration. We describe the photochemistry of a selection of novel α-keto carbamates as progenitors of reactive primary amines. The carbamates used in this study were chosen for detailed evaluation because of (1) their synthetic accessibility and (2) their ability to contribute to structure−activity relationships pertinent to base photogeneration. We seek to develop a basic understanding of the issues that determine the efficiency of amine photogeneration from 3′,5′-dimethoxybenzoin carbamates and substituted derivatives.

Results and Discussion

(1) Design Considerations. Previous experience in designing base photogenerators[6−8] suggests some of the most critical features to consider include the following: (1) favorable UV absorption characteristics, (2) quantum efficient photodecomposition, (3) solid-state photoreactivity, (4) photorelease of the base in a reactive form, (5) stability of photo byproducts, (6) thermal stability, and (7) ease of synthesis. This list is only a general guide because specific applications place additional custom requirements on any base photogenerator. As outlined in the introduction, several α-keto carbamates containing the 3′,5′-dimethoxybenzoin chromophore were chosen for evaluation as photobase precursors. The materials chosen for detailed study were restricted to the cyclohexylamine photogenerators shown in Scheme 2. By only selecting photoprecursors of cyclohexylamine, a direct comparison of the chromophore structure−photosensitivity relationship could be readily made. The α-keto carbamates of interest are those containing the following chromophores: the parent desyl group as in **1**, the 3,3′,5,5′-tetramethoxybenzoin moiety as in **2**, the 3′,5′-dimethoxybenzoin group as in **3**, the 3′,4,5′-trimethoxybenzoin moiety as in **4**, the 3′,5′-dimethoxy-4-methylthiobenzoin group as in **5**, 2-(3,5-dimethoxyphenyl)-1-(2-naphthalenyl)ethanone as in **6**, and 2,2-di-(3,5-dimethoxyphenyl)-1-phenylethanone as in **7**. These materials are characterized in terms of the design criteria outlined above. The preparation of the required benzoinyl chromophores was achieved using standard methods for benzoin synthesis. The photoactive cyclohexyl carbamates, **1**−**7**, were synthesized by reaction of the corresponding benzoin with cyclohexyl isocyanate. Representative synthetic details for the preparation of carbamates **4** and **7** are included in the Experimental Section. Full experimental data on the synthesis of several other novel benzoinyl chromophores and their elaboration to light sensitive carbamates will be reported elsewhere.[33]

(2) Photochemistry of Carbamates Derived from α-Hydroxy Ketones. These α-keto carbamates absorb UV light from just below 370 nm down to the deep UV. Excitation of the carbonyl chromophore is believed to cause photocyclization to the benzo[*b*]furan with concomitant liberation of the amine type base (Schemes 1 and 2). Due to the nature of the α-keto chromophore, UV exposure at longer wavelengths is thought to cause photocyclization via direct n−π^* excitation. However, photolysis at higher energy, via $\pi-\pi^*$ excitation, can also result in the liberation of base. A variety of spectroscopic methods e.g., ^{1}H NMR, IR, and UV proved useful in monitoring the photochemistry of these new base photogenerators. GC and GC-MS facilitated identification of the photoproducts.

(a) Solution Photosensitivity. (i) Photochemistry of Unsubstituted α-Keto Carbamates. Monitoring the photolysis of benzoin cyclohexyl carbamate (**1**) by a number of spectro-

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Table 1. NMR Monitoring of the Photogeneration of Cyclohexamine from Assorted Carbamates

carbamate	% conversion[a]	δ(3-Bf-H)[b]
benzoin (**1**)	75	not obsd
3,3′,5,5′-TetraMeO (**2**)	87	7.14
3′,5′-DiMeO (**3**)	93	7.12
3′,4,5′-TriMeO (**4**)	98	6.96
3′,5′-DiMeO-4-MeS (**5**)	37	7.07
3′,5′-DiMeO-2-Naphth (**6**)	62	7.25
2,2-Di-(3′,5′-MeO) (**7**)	62	not obsd

[a] Percent conversion calculated from the integral ratio of the photogenerated cyclohexylamine methine (CH, m, δ2.52) and the aromatic resonances after 60 min 350 nm Rayonet exposure. [b] Chemical shift for resonance of 3-H in benzofuran photoproduct in MeCN-d_3 quoted ppm downfield from TMS.

scopic methods served to indicate the complexity of the photochemistry of the α-keto chromophore. A significant conversion of benzoin cyclohexyl carbamate (**1**) to free cyclohexylamine was observed on monitoring the photolysis by ^{1}H NMR spectroscopy (Table 1). However, despite the high conversion, there was no evidence for photocyclization. In fact, the ^{1}H NMR spectrum became very complicated, implying that photodecomposition of this material proceeds by a variety of competing pathways. This was further confirmed by monitoring the photolysis of benzoin carbamate (**1**) by infrared spectroscopy. In this case, the keto carbonyl stretch (1699 cm^{-1}) disappears, while the carbamate carbonyl stretch (1722 cm^{-1}) remains substantially intact. A weak carbonyl stretch at 1658 cm^{-1} also appears possibly due to photooxidation. These observations are consistent with photodecomposition of benzoin carbamate (**1**) proceeding by a variety of mechanisms of which photocyclization to benzo[*b*]furan plays only a minor role. Furthermore, a complex multicomponent mixture is observed by TLC after 350 nm photolysis of benzoin carbamate (**1**).

(ii) Photochemistry of Aryl Substituted α-Keto Carbamates. The importance of meta activation by 3′,5′-dimethoxy substituents in the photocyclization of α-keto carbamates to benzo[*b*]furans is apparent in the 350 nm solution photolysis of α-keto carbamates, **1**−**7**, as monitored by ^{1}H NMR spectroscopy in dry, degassed acetonitrile-d_3. Table 1 shows examples of α-keto carbamates which undergo efficient photogeneration of cyclohexylamine on 350 nm photolysis. For all these carbamates, the integral of the carbamate cyclohexyl methine [cyclohexyl CH, m, δ ∼3.2−3.4 (dependent on the structure of photosensitive carbamate)] decreased, while the expected multiplet of the cyclohexyl methine of free cyclohexylamine appeared at δ 2.52, with increasing 350 nm exposure in a Rayonet photochemical reactor. The ratio of the cyclohexyl methine integral for free cyclohexylamine to the aryl resonances gave the percent conversion after 60 min. The percent conversion was calculated for the α-keto carbamates, shown in Table 1, and was found to vary from 37−98% depending on the chromophore structure. Besides identifying cyclohexylamine, ^{1}H NMR spectroscopy allowed the expected benzo[*b*]furan to be identified as the major photo by-product on 350 nm photolysis of 3′,5′-dimethoxy substituted benzoin carbamates, **2**−**6**. A characteristic singlet of the 3-benzo[*b*]furan proton in the photoproduct mixture appears with increasing photolysis. The chemical shift of this proton is included in Table 1. In these systems which undergo smooth photocyclization, the percent conversion for formation of benzo[*b*]furan tends to parallel that for amine generation. The cleanliness of the photocyclization of these 3′,5′-dimethoxy activated benzoin carbamates is nicely illustrated by following the changes in the ^{1}H NMR aryl resonances with increasing exposure dose for the conversion of carbamate (**2**) to benzo[*b*]furan (**2a**) in tetrahydrofuran-d_8 (Figure 1).

A plot of percent conversion conversion against irradiation time for the 350 nm photolysis of carbamate **2** further demonstrates the efficiency of the benzoin photocyclization (Figure 2). The same clean photochemistry is not apparent with other α-keto carbamates. For instance, systems lacking the 3′,5′-dimethoxy substitution pattern e.g., **1** undergo particularly complex photodecomposition.

The clean photogeneration of free cyclohexylamine from all 3′,5′-dimethoxy substituted benzoin carbamates was further confirmed by both gas chromatography using coinjection and GC-MS studies ($C_6H_{11}NH_2$ $M^+ = 99$). For the cyclohexyl carbamates, **2**−**6**, GC-MS indicated the major byproducts were the expected substituted benzo[*b*]furans, **2a**−**6a**, respectively. Other minor products were identified as the corresponding desoxybenzoin e.g., **2b**, the corresponding substituted benzil e.g., **2c**, the corresponding *N*-acylcyclohexylamine e.g., **2d** and dicyclohexylurea (Scheme 2). While the mechanism for formation of these trace photoproducts is unknown their presence may, in some cases, be rationalized in terms of known benzoin photochemistry. For instance, the desoxybenzoin **2b** may be formed by loss of the carbamoyloxy moiety. This mode of photocleavage is common in benzoin photochemistry and tends to occur when a good leaving group is present at the α-keto position. Indeed, the photolabile phenacyl protecting group is known to cleave via this pathway.[34] The benzil photoproduct (**2c**) may be formed by cleavage of the oxycarbonyl bond followed by photooxidation. In the case of unsymmetrical benzoin carbamates, only the corresponding unsymmetrical benzil was identified by GC-MS. Since there was no indication of any symmetrical benzils, formation of these 1,2-ethanediones is unlikely to be the product of acyl radical recombination. Similar cleavage of oxycarbonyl bonds is known to occur in some benzoin esters. For instance, photolysis of 4,4′-dimethoxybenzoin acetate is known to form 4,4′-dimethoxybenzil as the major product.[16] Furthermore, benzil was recently found to be the major photoproduct from photolysis of the α-glutamic ester of benzoin.[21] Tentatively, the formation of *N*-acylcyclohexylamine (**2d**) may be considered to proceed in the following manner. The *N*-acylcyclohexylamine (**2d**) may be formed by the combination of acyl and cyclohexylamino radicals. The acyl radicals could be formed by the well-known Norrish Type I photocleavage of benzoins.[35] Cyclohexylamino radicals may be formed in a number of ways. For example, the carbamoyloxy radicals liberated during formation of the desoxybenzoin **2b** could undergo facile decarboxylation. Alternatively, cleavage of the oxycarbonyl bond to give the substituted benzil (**2c**) would be accompanied by formation of a *N*-formylcyclohexylamino radical. This species could possibly liberate cyclohexylamino radicals via decarbonylation. Interestingly, no indication of the corresponding aldehyde from the acyl radical formed by Norrish Type 1 cleavage was available by GC-MS. This implies recombination of acyl and amino radicals is strongly favored over hydrogen abstraction. The presence of trace amounts of dicyclohexylurea may be tentatively rationalized as follows. Combination of *N*-formylcyclohexylamino and cyclohexylamino radicals would give dicyclohexylurea. Another possibility is

(34) Sheehan, J. C.; Umezawa, K. *J. Org. Chem.* **1973**, *38*, 3771. Church, G.; Ferland, J. M.; Gauthier, J. *Tetrahedron Lett.* **1989**, *30*, 1901.

(35) Schonberg, A.; Fateen, A. K.; Omran, S.; *J. Am. Chem. Soc.* **1956**, *78*, 1224. Lewis, F. D.; Lauterbach, R. T.; Heine, H. G.; Hartmann, W.; Rudolph, H. *J. Am. Chem. Soc.* **1975**, *97*, 1519. de Mayo, P.; Nakamura, A.; Tsang, P. W. K.; Wong, S. K. *J. Am. Chem. Soc.* **1982**, *104*, 6824. Dasaratha Reddy, G.; Usha, G.; Ramanathan, K. V.; Ramamurthy, V. *J. Org. Chem.* **1986**, *51*, 3085. Dasmohapatra, G.; Wolff, T.; *J. Photochem. Photobiol. A: Chem.* **1992**, *69*, 209.

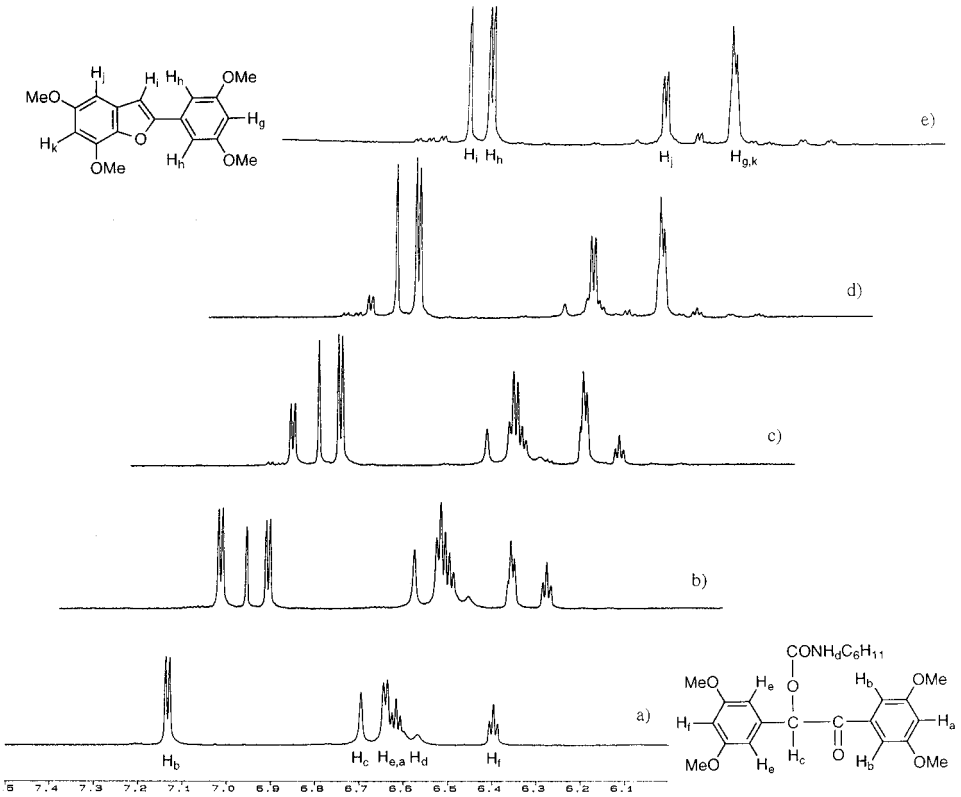


Figure 1. Change in ^{1}H NMR aromatic resonances of carbamate (**2**) as a 38.6 mM solution in THF-d_8 with increasing 350 nm photolysis in Rayonet: (a) prior to exposure, (b) after 15 min exposure, (c) after 30 min exposure, (d) after 60 min exposure, and (e) after 90 min exposure.

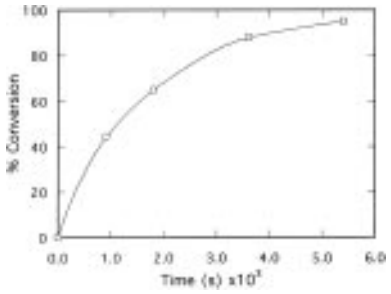


Figure 2. Plot of percent conversion against exposure time for carbamate (**2**) as a 38.6 mM solution in THF-d_8 on 350 nm exposure in Rayonet.

the reaction of photogenerated cyclohexylamine with cyclohexyl isocyanate. The intermediate isocyanate could be formed by loss of a hydrogen atom from a *N*-formylcyclohexylamino radical.

Further evidence for the photochemical rearrangement of these α-keto carbamates was obtained by following the changes in the infrared spectrum of a solution of carbamate (**3**) in dry acetonitrile with increasing UV exposure dose. As seen in Figure 3, 350 nm Rayonet exposure of carbamate (**3**) caused the gradual disappearance both the keto carbonyl stretch (1700 cm^{-1}) and the carbamate carbonyl stretch (1723 cm^{-1}). This change is consistent with the proposed mode of photodecomposition (Scheme 2) in which photocyclization to liberate the free amine causes these stretches to disappear.

In addition, evidence for the photogeneration of free amine was gained by monitoring the changes in the N−H stretching frequency of this substrate (**3**) (Figure 4). In this case, UV exposure at 350 nm resulted in the gradual depletion of the carbamate N−H stretch at 3360 cm^{-1}, with concomitant appearance of stretches due to the photogenerated cyclohexylamine in the 3500−3700 cm^{-1} region. Similar disappearance of both carbonyl stretches was observed on irradiation of carbamates (**2**) and (**4**). These findings are consistent with smooth photocyclization and concomitant amine liberation occurring in these 3′,5′-dimethoxy substituted benzoin carbamates. In the case of carbamates, **5** and **6**, the disappearance of both carbonyl groups was complicated by the appearance of two weak absorptions at 1675 and 1685 cm^{-1}, respectively. This indicates the photocyclization of carbamates, **5** and **6**, is complicated by side reactions open to the desyl chromophore. These include photocleavage by Norrish Type I and C−O homolytic pathways, both of which would produce carbonyl containing products.[34,35] Such competing photochemistry may also explain the slightly lower yields for amine generation from carbamates (**5**) and (**6**) (Table 1).

Beyond 350 nm, the extinction coefficients of these carbamates are typically of the order 50−200 L mol^{-1} cm^{-1}. However, it should be noted that the efficiency of photocyclization and concomitant amine generation using 350 nm Rayonet lamps is not solely dependent on the absorption of these carbamates at 350 nm. Rather, Rayonet lamps are known to be nonmonochromatic and therefore, there is significant overlap between the short wavelength lamp output and the long wavelength absorption of the benzoin chromophore. Indeed, carbamates which absorb the most light at longer wavelengths are not the most efficient according to ^{1}H NMR studies. For instance, conversion of carbamate (**6**) ($\epsilon_{(365)}$ 212 L mol^{-1} cm^{-1}) to free cyclohexylamine only reached 62%, while carbamate (**2**) ($\epsilon_{(365)}$ 45 L mol^{-1} cm^{-1}) showed around 87% conversion (Table 1) under identical conditions. This indicates a subtle relationship exists between photocyclization and the nature of the benzoyl chromophore.

The UV absorbance data of carbamates, **1**−**7**, is summarized in Table 2. Table 2 indicates that the UV absorption of these photoactive carbamates may be tailored through substituent effects, and therefore these materials may be optimized for particular applications. Most notably, the use of chromophores

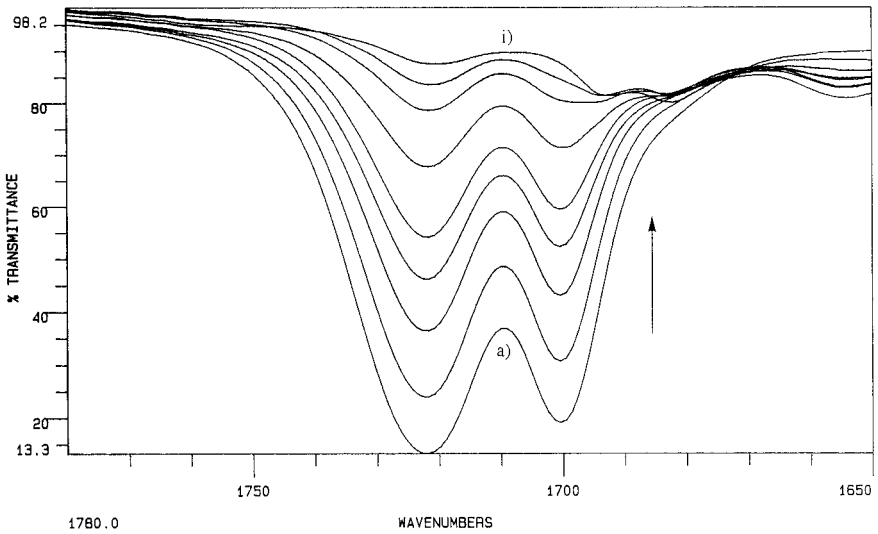


Figure 3. Change in carbonyl region of carbamate (**3**) as a 11.8 mM solution in MeCN with increasing 350 nm photolysis in Rayonet: (a) prior to exposure, (b) after 5 min exposure, (c) after 10 min exposure, (d) after 15 min exposure, (e) after 20 min exposure, (f) after 30 min exposure, (g) after 45 min exposure, (h) after 60 min exposure, and (i) after 120 min exposure.

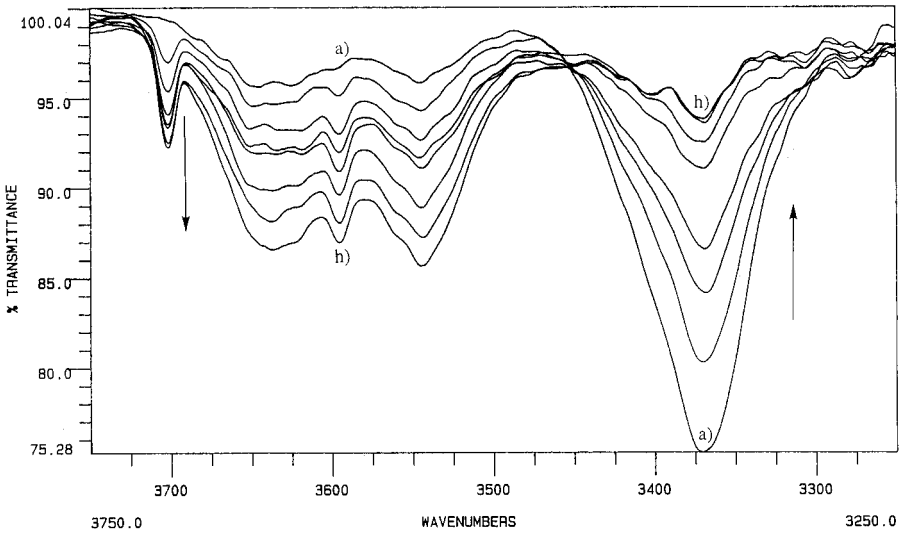


Figure 4. Change in N−H stretching region of carbamate (**3**) as a 11.8 mM solution in MeCN with increasing 350 nm photolysis in Rayonet, (a) prior to exposure, (b) after 5 min exposure, (c) after 10 min exposure, (d) after 15 min exposure, (e) after 30 min exposure, (f) after 60 min exposure, (g) after 120 min exposure, and (h) after 240 min exposure.

Table 2. UV Absorbance Data on Substituted Benzoin Carbamates

carbamate	ϵ_{254}	ϵ_{313}	ϵ_{336}
benzoin (**1**)	9366	279	296
3,3′,5,5′-TetraMeO (**2**)	6180	2195	1701
3′,5′-DiMeO (**3**)	12341	516	311
3′,4,5′-TriMeO (**4**)	7450	930	375
3′,5′-DiMeO-4-MeS (**5**)	2794	20935	5049
3′,5′-DiMeO-2-Naphth (**6**)	37252	1850	2008
2,2-Di-(3′,5′-MeO) (**7**)	11501	328	169

[a] Molar extinction coefficients ($L \cdot mol^{-1} \cdot cm^{-1}$) calculated from Beer−Lambert plot created by serial dilution.

containing bathochromic substituents allows the UV spectrum of the photoactive carbamates to be manipulated out to approximately 340 nm. For example, the 4-thiomethyl substituted carbamate (**5**) and the 1-naphthalenyl carbamate (**6**) have extinction coefficients at 336 nm of 5049 and 2008 L mol^{-1} cm^{-1}, respectively (Table 2). Therefore, it is apparent that structural variation of the benzoyl chromophore does affect the long wavelength absorption. However, in these systems the absorption drops off quickly beyond 340 nm, and the substituent effect is not strong enough to cause the desired bathochromic shift out to 350 nm.

The result of following the changes in the UV spectrum of a dilute solution of carbamate (**2**) upon 350 nm exposure is shown in Figure 5. Three isobestic points are observed: 251, 266, and 340 nm respectively. Overall, the change in the UV spectrum is representative of this class of α-keto carbamates. The observed UV spectral changes are in agreement with the other spectral evidence that suggests that photogeneration of the free amine is accompanied by photocyclization to form the corresponding benzo[*b*]furan (**2a**) (Scheme 2).

During irradiation of carbamate (**2**), the absorption maximum originally at 267 nm is replaced by an intense absorption at 300 nm, due to photocyclization to the conjugated benzo[*b*]-furan (**2a**). Interestingly, the absorption due to the aryl $\pi-\pi^*$ transition (250−265 nm) decreases on photocyclization. Furthermore, beyond 340 nm, the absorption tail of the carbonyl chromophore disappears with increasing 350 nm exposure. This bleaching of the long wavelength $n-\pi^*$ transition was only observed for 3,3′,5,5′-tetramethoxybenzoin carbamate (**2**). Other derivatives, e.g., **3** and **6**, only show bleaching of the deep UV

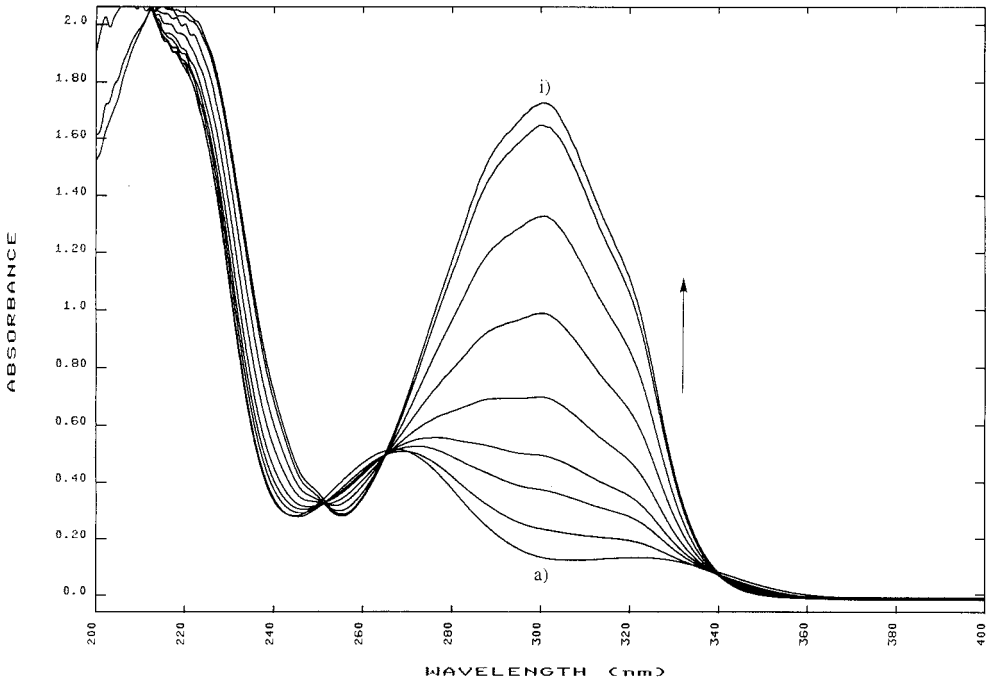


Figure 5. Change in UV spectrum of carbamate (**2**) as a 6.164×10^{-5} M solution in MeCN with increasing 350 nm photolysis. (a) Prior to exposure, (b) after 15 s exposure, (c) after 30 s exposure, (d) after 45 s exposure, (e) after 75 s exposure, (f) after 120 s exposure, (g) after 180 s exposure, (h) after 300 s exposure, and (i) after 450 s exposure.

$\pi-\pi^*$ absorption while carbamates, **4** and **5**, show antibleaching. The propensity for bleaching of both the long wavelength tail (>340 nm) and the deep UV absorption (@ 250−265 nm) is a particularly attractive feature of this photogenerator (**2**). Based on the observed photobleaching of carbamate (**2**), this material holds particular promise as a photocatalyst in thick film applications at both deep UV and far UV exposure wavelengths. This is in contrast to the *o*-nitrobenzyl derived class of photobase generators in which antibleaching has restricted their use in some applications. The overlay plot (Figure 5) generated on solution photolysis of α-keto carbamate (**2**) is similar to that reported by Sheehan *et. al.*[17] for 3′,5′-dimethoxybenzoin acetate. While the mechanism of photocyclization may differ, the similarity of the UV spectral data is consistent with the 3′,5′-dimethoxybenzoin chromophore undergoing the same photochemical rearrangement to form benzo[*b*]furan (**2a**) for both esters and carbamates. The photolysis of 3′,5′-dimethoxy substituted carbamates, **2**−**6**, is remarkably clean by TLC. In these instances, the respective benzo[*b*]furans, **2a**−**6a**, are the major products, and only trace amounts of other byproducts are present.

Preparative Photolysis. Preparative photolysis of cyclohexyl carbamates of both 3,3′,5,5′-tetramethoxybenzoin (**2**) and 3′,5′-dimethoxybenzoin (**3**) proceeded smoothly in acetonitrile. In both cases, the major products were cyclohexylamine and the appropriate substituted benzo[*b*]furan, **2a** and **3a**, respectively. The fluorescent benzo[*b*]furans were isolated as the major photoproducts in excellent yields (80−85%) by flash chromatography. In the case of 3,3′,5,5′-tetramethoxybenzoin cyclohexyl carbamate (**2**), a deoxybenzoin photoproduct (**2b**), formed by loss of the carbamoyloxy moiety, was also isolated in 7% yield from the photolysate. Formation of such products has also been observed during GC-MS product studies (vide supra). Comparison of the extinction coefficients of the starting carbamates with the respective benzo[*b*]furan photoproducts indicates that the photoproducts absorb significantly less light in the 250−265 nm region. For example, the extinction coefficient of 3′,5′-dimethoxybenzoin cyclohexyl carbamate (**3**) at 254 nm is 12 341 L mol^{-1} cm^{-1}, while that of 2-phenyl-5,7-dimethoxybenzo[*b*]furan (**3a**) is 5972 L mol^{-1} cm^{-1}. This difference explains the deep UV photobleaching of these photoactive carbamates.

(iii) Photochemistry of 2,2-Disubstituted α-Keto Carbamates. By ^{1}H NMR spectroscopy, the 2,2-diaryl substituted cyclohexyl carbamate (**7**) was observed to photoliberate a significant amount of free cyclohexylamine (Table 1). However, no evidence for the formation of benzo[*b*]furan (**7a**) was available by ^{1}H NMR spectroscopy because the spectrum became very complex . By GC-MS, only cyclohexylamine, dicyclohexylurea, and *N*-benzoylcyclohexylamine could be identified. Infrared spectroscopy indicated that photocyclization proceeds somewhat slowly, with both the keto carbonyl stretch at 1700 cm^{-1} and the carbamate carbonyl stretch at 1727 cm^{-1} slowly disappearing on 350 nm Rayonet exposure. However, the rate of disappearance of the keto carbonyl stretch is faster than the carbamate carbonyl stretch and a weak absorption appears at 1685 cm^{-1}. Overall, photolytic studies on the 2,2-disubstituted α-keto carbamate (**7**) resemble the less efficient 3′,5′-dimethoxybenzoin carbamates (**5**) and (**6**). Based on these experimental observations, it seems likely that 2,2-disubstituted α-keto carbamates undergo amine photogeneration via a number of competing pathways, in which photocyclization plays only a minor role.

(b) Solid-State Photosensitivity. (i) Photochemistry of Unsubstituted α-Keto Carbamates. Interestingly, benzoin cyclohexyl carbamate (**1**) has previously been reported to be an efficient base photogenerator for deep UV lithography.[36] In contrast, our results upon monitoring the solution photochemistry of this class of benzoin derived base photogenerator suggested photocylization was only a minor photodecomposition pathway (vide supra). Based on this observation, the solid state photodecomposition of this α-keto carbamate was investigated in limited detail. The solid state photoreactivity was conveniently monitored by irradiating thin poly(methacrylonitrile) (PMAN) films containing a few mol % benzoin carbamate (**1**) and following the changes in the UV spectrum. PMAN was selected as the polymer matrix for several reasons. First, good

(36) Winkle, M. R. Eur. Patent 0 425 142 A2, 1991; *Chem. Abstr.* **1991**, *116*, 48918w.

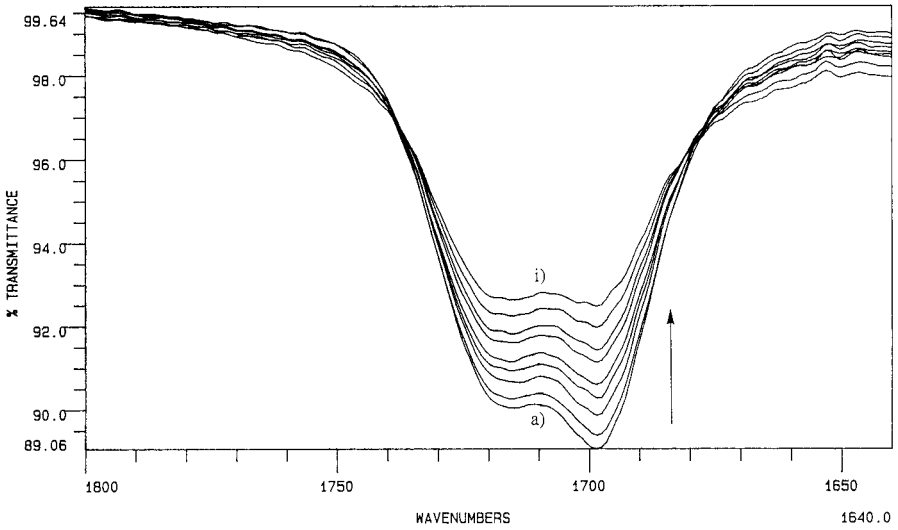


Figure 6. Change in IR spectrum of carbamate (**2**) (5.36 mol%) in a 1.265 μm thick PMAN film with increasing 254 nm exposure dose: (a) prior to exposure, (b) after 50 mJ cm^{-2} exposure, (c) after 100 mJ cm^{-2} exposure, (d) after 200 mJ cm^{-2} exposure, (e) after 300 mJ cm^{-2} exposure, (f) after 400 mJ cm^{-2} exposure, (g) after 500 mJ cm^{-2} exposure, (h) after 750 mJ cm^{-2} exposure, and (i) after 1.0 J cm^{-2} exposure.

optical quality films of PMAN may be readily cast. Second, PMAN films are UV transparent in the area of interest. Third, PMAN is relatively inert and therefore does not interfere with the photochemical reaction to generate amines. The observed change in the UV spectrum of these thin films is inconsistent with efficient photocyclization to form the corresponding benzo[*b*]furan (**1a**), because the long wavelength n$-\pi^*$ transition of the carbonyl chromophore does not disappear. This observation is in agreement with the solution IR study, in which both carbonyl absorptions did not disappear during UV exposure. Therefore, based on the proven utility of benzoin cyclohexyl carbamate (**1**) as a base photogenerator,[36] the mechanism of cyclohexylamine photogeneration most likely proceeds via several alternate pathways among which photocyclization plays only a minor role. Despite the complex solid state photochemistry of (**1**), its utility as a base photogenerating material for deep UV lithographic applications is likely further increased by virtue of the observed bleaching at 254 nm.

(ii) Photochemistry of Aryl Substituted α-Keto Carbamates. The intramolecular nature of the photocyclization of 3′,5′-dimethoxy substituted benzoins suggests that photogeneration of amines can be performed in the solid state. This proved to be the case with all benzoin carbamates containing this substitution pattern undergoing photodecomposition as monitored by infrared and UV spectroscopy. The solid state photoreactivity was established by coating sodium chloride and quartz substrates with 1 μm thick PMAN films containing approximately 5 mol % of the benzoin carbamate and irradiating these films at various wavelengths.

Photocyclization was monitored using infrared spectroscopy to follow the simultaneous disappearance of both keto and carbamate carbonyl absorptions with increasing UV exposure dose. Photocyclization to liberate base was found to be general in nature and occurred on irradiation over a broad range of wavelengths ranging from deep UV to far UV. For instance, 3,3′,5,5′-tetramethoxybenzoin carbamate (**2**) undergoes photocyclization to liberate cyclohexylamine on irradiation with either 254, 313, 336, or 365 nm light. The observed change in the infrared spectrum on 254 nm photolysis of such films is illustrated for the photocyclization of α-keto carbamate (**2**) (Figure 6). There is a substantial difference in the extinction coefficients at 254 and 365 nm in these carbamates. For example, the extinction coefficient of carbamate (**2**) at 254 nm is 6180 L mol^{-1} cm^{-1}, while at 365 nm it is 102 L mol^{-1} cm^{-1}. In @ 1 μm thick PMAN films containing 5 mol % of carbamate (**2**), this amounted to absorption of 78.8% of the light at 254 nm and only 7.1% of the light at 365 nm. However, despite the low absorption at 365 nm, the photochemistry proceeds smoothly at these long wavelengths (vide infra).

The result of following the changes in the UV spectrum of thin films of PMAN containing about 5 mol % α-keto carbamate (**3**) on 254 nm exposure is shown in Figure 7. The deep UV maximum @ 245 nm is replaced by an intense absorption maximum at 300 nm. The change in the UV spectrum is representative for this class of α-keto carbamates and is consistent with photocyclization to the conjugated benzo[*b*]furan taking place in the solid state. This spectral change is accompanied by bleaching of the deep UV $\pi-\pi^*$ absorption in the region 250−265 nm. Such bleaching is desirable in many applications and many of these base photogenerators hold significant promise as photocatalysts particularly in thick film applications where photobleaching at the exposure wavelength is critical.

Furthermore, the similarity between the solid state and the solution photolyses, as monitored by IR and UV spectroscopy, implies the photochemistry is not appreciably altered in the solid state. This consideration is of importance in extending the utility of these base photogenerators to a variety of solid state applications.

(3) Quantum Yield. In the interest of evaluating the quantum yield for photocyclization over a range of common UV exposures wavelengths, we were most interested in looking at α-keto carbamates which possessed favorable UV characteristics in the range 250−400 nm. In this regard, 3,3′,5,5′-tetramethoxybenzoin cyclohexyl carbamate (**2**) was considered a particularly attractive candidate because it possessed a weak but bleachable UV absorption which extended beyond 350 nm. Accordingly, the solid state quantum yield for the photodecomposition of 3,3′,5,5′-tetramethoxybenzoin cyclohexyl carbamate (**2**) was evaluated at 254, 313, 336, and 365 nm. The method used to determine the solid state photoefficiency is based on an infrared spectroscopic method originally developed by Pitts *et al.*[37] This technique was further developed by Reichmanis *et al.*[38] to determine the solid state quantum yields of *o*-

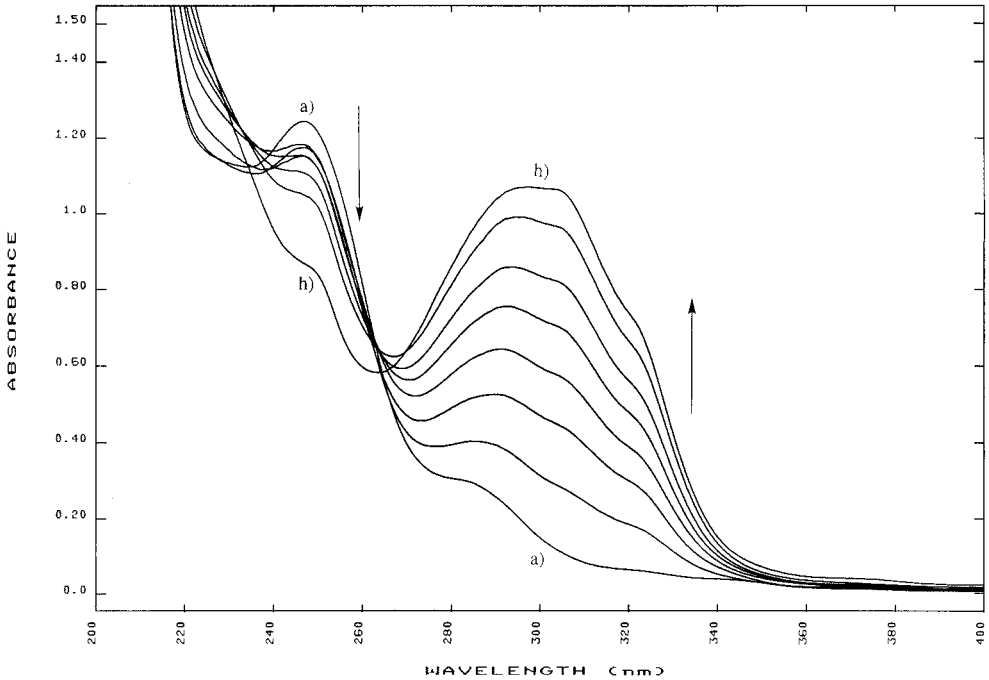


Figure 7. Change in UV spectrum of carbamate (**3**) (4.67 mol %) in a 1.375 μm thick PMAN film with increasing 254 nm exposure dose: (a) prior to exposure, (b) after 30 mJ cm^{-2} exposure, (c) after 75 mJ cm^{-2} exposure, (d) after 125 mJ cm^{-2} exposure, (e) after 200 mJ cm^{-2} exposure, (f) after 300 mJ cm^{-2} exposure, (g) after 500 mJ cm^{-2} exposure, and (h) after 1.0 J cm^{-2} exposure.

Table 3. Quantum Yields[a] for the Photocyclization of 3,3′,5′-Tetramethoxybenzoin Carbamate (**2**) (with Concomitant Liberation of Cyclohexylamine

Φ_{254nm}	Φ_{313nm}	Φ_{336nm}	Φ_{365nm}
0.067	0.080	0.054	0.028

[a] Quantum yield evaluated from a plot of log Φ versus the number of quanta absorbed, by back extrapolation to zero quanta absorbed, from data taken at conversion values unaffected by the inner filter effect.

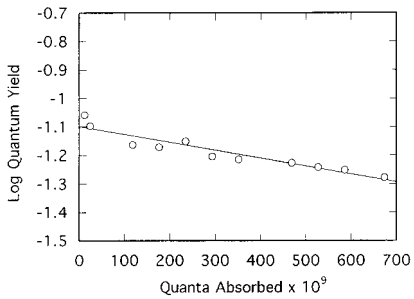


Figure 8. Plot of log quantum yield against number of quanta absorbed for 365 nm exposure of carbamate (**2**) (5.36 mol %) in a 1.265 μm thick PMAN film.

nitrobenzyl esters in polymer films. More recently, we have used this method to measure the photoefficiency of assorted amine progenitors in thin film coatings.[7−9] The experimentally determined quantum yields for the photodecomposition of 3,3′,5,5′-tetramethoxybenzoin cyclohexyl carbamate (**2**) are shown in Table 3 and were found to range from 0.03 to 0.08 depending on the exposure wavelength.

In strict terms, these quantum yields are for the disappearance of the starting α-keto carbamate (**2**). However, the quantum yields may be assumed to be representative of cyclohexylamine photogeneration. This assumption is considered valid because carbamate (**2**) has demonstrated clean generation of cyclohexylamine and benzo[*b*]furan (**2a**), uncomplicated by side products, based on ^{1}H NMR analysis of solution photolysates at low conversion. The quantum yields were evaluated at low percent conversion (5−25%) by back extrapolating a plot of log quantum yield against number of quanta absorbed, to the point of zero quanta absorbed. Figure 8 illustrates the result of the quantum yield determination upon 313 nm irradiation of 3,3′,5,5′-tetramethoxybenzoin cyclohexyl carbamate (**2**).

The apparent wavelength dependence of the solid state quantum yields is particularly interesting. A similar wavelength dependence has been observed in the case of *o*-nitrobenzyl ester photochemistry where solid state quantum yields at 313 nm were typically higher than those at 254 nm.[38] Such variations of quantum yield with exposure wavelength are suggestive of selective access to excited states. In the absence of experimental data in this area, our preliminary solid state photoefficiency data may tentatively be correlated to the absorbance spectra of the keto chromophore. Most notably, the quantum yield is greatest at 313 nm which closely corresponds to the absorbance maximum of the carbonyl chromophore. This suggests that photocyclization proceeds most efficiently via direct n−π* excitation of the keto moiety. Assuming that photocyclization only proceeds via excitation of the keto carbonyl group then exposure at other wavelengths may be speculated as being less efficient since some additional process may be required to effect carbonyl n−π* excitation. The results of our preliminary solid state quantum yield determination suggest that direct excitation of the carbonyl group is the preferred pathway for photocleavage.

The preliminary solid state quantum yield values for amine photogeneration are significantly lower than that reported for the photoliberation of acetate and phosphate in solution.[17,25−28] This result can be rationalized as follows. First, reduced molecular motion in the solid state probably increases the difficulty of attaining appropriate conformations for photore-

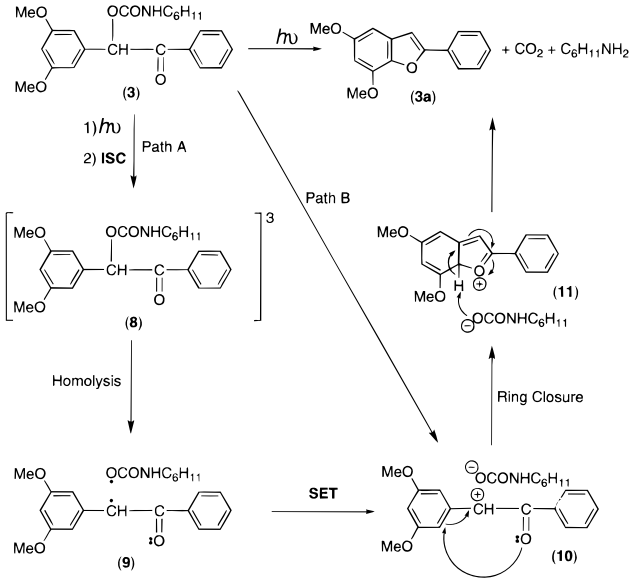
(37) Pitts, J. N., Jr.; Wan, J. K. S.; Schuck, E. A. *J. Am. Chem. Soc.* **1964**, *86*, 3606. Cowell, G. W.; Pitts, J. N., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 1106.

(38) Reichmanis, E.; Gooden, R.; Wilkins, C. W., Jr.; Schonhorn, H. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1075. Reichmanis, E.; Smith, B. C.; Gooden, R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1. Houlihan, F. M.; Shugard, A.; Gooden, R.; Reichmanis, E. *Macromolecules* **1988**, *21*, 2001.

action.[38] Second, phosphate and acetate may be expected to be better leaving groups than the carbamoyloxy moiety. Evidence of the leaving group ability of these groups is provided by comparison of the pK_a values for the corresponding conjugate acids. The pK_a of an alkyl carbamic acid is 5.25[39] which indicates this moiety is likely to be a poorer leaving group than both acetate (pK_a 4.76) and diethylphosphate (pK_a 1.39).[40]

While the mechanism of amine photogeneration from 3′,5′-dimethoxybenzoin carbamates is not the primary focus of this work, it certainly merits some discussion. Since the photocleavage mechanism of benzyl esters, carbonates, and carbamates are similar,[41] details of the mechanism of amine photogeneration from benzoin carbamates may, in part, be elucidated from prior mechanistic work on photocyclization of substituted benzoins. In the case of benzoin phosphate, photocleavage is quenched by common triplet quenchers indicating that the reaction proceeds via the triplet manifold.[25] On the other hand, the photocleavage of carboxylate and phosphate esters of meta methoxy activated benzoins is not quenched by piperylene[17] or naphthalene.[18] This suggests that photocleavage in meta methoxy substituted benzoins proceeds via a singlet excited state or via a short lived triplet state. Based on the available mechanistic data, Givens *et al.*[21,25] have proposed an ion-pair mechanism to explain the photocyclization of desyl esters. This mechanism may be extended to rationalize the photogeneration of amines from 3′,5′-dimethoxybenzoin carbamates, as shown by path A in Scheme 3. On irradiation, n−π* excitation of the carbonyl group leads to formation of the triplet excited state (**8**). Subsequent homolysis produces a radical pair (**9**) which undergoes rapid electron transfer to yield an ion pair (**10**). After ring closure, the liberated anion acts as a base and removes the bridgehead proton from (**11**), forming the benzo[*b*]furan photoproduct. The unstable carboxylated amine then loses carbon dioxide, liberating the free amine. The benzylic carbocation intermediate (**10**) is postulated based on the photochemical meta effect.[42] In the photochemically excited state, meta methoxy groups are known to be particularly efficient in stabilization of a developing positive charge at a benzylic site. In methoxy substituted benzenes, the electron density meta to the methoxy substituents is enhanced in the singlet excited state relative to the meta sites in the ground state. Since the photocyclization pathway is the preferred mode of photocleavage for 3′,5′-dimethoxybenzoinyl carbamates, it seems probable that photocyclization proceeds via a meta benzylic carbocation as shown in Scheme 3. Consistent with the meta effect, an alternative mechanism for cleavage of 3′,5′-dimethoxybenzoin esters and phosphates has recently been proposed.[18] This mechanism is based on classical photosolvolysis and is consistent with the observation that the reaction likely proceeds via a singlet state.[43] In the case of 3′,5′-dimethoxybenzoin carbamates, this pathway is represented by path B in Scheme 3. Recently, Pincock and co-workers[44] have suggested that direct heterolytic cleavage to form an ion pair is only a minor pathway but rather, the

Scheme 3



photochemistry of meta methoxy substituted benzylic esters involves competition between pure homolysis and homolysis followed by electron transfer to give an ion pair. In light of the competitive homo-/heterolytic cleavage type mechanism proposed for methoxy substituted benzylic esters, the origin of the experimentally observed meta effect in photosolvolytic reactions has been re-examined by modern day computational methods.[45] This study revealed heterolysis in the singlet excited state of simple 3,5-dimethoxybenzylic systems is favored over homolysis by about 32 kcal mol^{-1} and therefore reaffirmed the existence of the photochemical meta effect. Another important mechanistic point to consider is that photocleavage of the related phenacyl protecting group is known to proceed by C-O homolysis followed by radical combination.[34] In the case of the benzoinyl chromophore, this mechanism would involve homolysis to form a radical which can abstract a hydrogen atom from the solvent to give a deoxybenzoin product. Indeed, a small amount of the desoxybenzoin product (**2b**) was isolated from the photolysate of 3′,5′-dimethoxybenzoin carbamate (**2**). This indicates the C−O homolysis/radical combination mechanism only plays a minor role in the photocleavage of meta methoxy substituted benzoin carbamates. Based on all the evidence, the predominant mechanism for photocyclization in 3′,5′-dimethoxybenzoin carbamates most likely involves direct heterolytic cleavage as shown in path B, Scheme 3. This mechanism is consistent with the photochemical meta effect and has previously been proposed for the photocyclization of analogous benzoin esters.[18,43]

Related mechanistic arguments may also be used to explain the enhanced photocyclization yields observed in other meta methoxy substituted benzoinyl carboxylate esters.[16−18] In contrast, the photochemistry afforded by benzoinyl phosphate seems to be unique in undergoing efficient photocyclization without meta stabilization.[25] The differences outlined above indicate the nature of the leaving group as well as the structure of the benzoinyl chromophore play an integral role in determining the photocleavage mechanism of substituted benzoins. Indeed, benzoin esters of α- and γ-glutamic acid have been shown to undergo photocleavage via vastly different pathways.[21]

(4) Thermal Stability. For benzoin carbamates to be potentially useful in the formulation of resist materials or

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(41) Parman, T.; Pincock, J. A.; Wedge, P. J. *Can. J. Chem.* **1994**, *72*, 1254.
(42) Zimmerman, H. E. In *Advances in Photochemistry*; Noyes, W. A., Jr., Hammond, G. S., Pitts, J. N., Jr. Eds.; Interscience: New York, 1963; Vol. 1, p 183.
(43) A referee correctly stated that the absolute assignment of the photocyclization reaction as being a singlet sate process can only be done with certainty by combining quenching data with sensitization experiments or with the direct spectroscopic detection of the reactive excited state. Our present assignment of singlet state reactivity is tentatively made in the absence of any further information to support the original quenching data of Sheehan[17] and Pirrung.[18]
(44) Pincock, J. A.; Wedge, P. J. *J. Org. Chem.* **1994**, *59*, 5587. Hilborn, J. W.; MacKnight, E.; Pincock, J. A.; Wedge, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 3337.
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Table 4. Thermal Properties of Substituted Benzoin Carbamates

carbamate	melting point (°C)	dec temp[a] (°C)
benzoin (**1**)	87−88	193
3,3′,5,5′-TetraMeO (**2**)	116−118	233
3′,5′-DiMeO (**3**)	149−151	203
3′,4,5′-TriMeO (**4**)	105−107	218
3′,5′-DiMeO-4-MeS (**5**)	152−154	252
3′,5′-DiMeO-2-Naphth (**6**)	161−162	230
2,2-Di-(3′,5′-MeO) (**7**)	170−172	231

[a] Decomposition temperature was taken as the temperature of 5% weight loss as determined by thermogravimetric analysis (in air).

imaging systems, they must be thermally stable under standard lithographic processing conditions that may include prolonged heating at temperatures as high as 150 °C. The thermal properties of these α-keto carbamates were determined by a combination of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). As shown in Table 4, this requirement was readily satisfied for carbamates derived from α-hydroxy ketones.

The decomposition temperature was determined by TGA, which shows that near quantitative weight loss occurs on heating carbamate (**2**) above 290 °C in a nitrogen atmosphere. In an air atmosphere, the decomposition temperature is approximately 60 °C lower for carbamate (**2**) (Table 4). Furthermore, it is known that many common photoacid generators exhibit decreased thermal stability in a phenolic matrix.[46] In contrast, these base photogenerators retain their thermal stability in a phenolic environment. For instance, both the melting point and decomposition temperature of carbamate (**2**) were only lowered by 5 °C on mixing with poly(vinyl phenol) as determined by DSC. Because of their thermal stability, these materials offer a potential advantage over many common photocatalysts used in microlithography and polymer curing applications.

Conclusions

Substituted benzoin carbamate derivatives of amines show great potential as photoprecursors of organic bases. These α-keto carbamates are cleaved by UV irradiation below 370 nm down to the deep UV both in solution and in the solid state. The substitution pattern on the aryl rings and at the 2-position was varied to determine the optimal chromophore structure. Cyclohexyl carbamates derived from 3′,5′-dimethoxybenzoin and its substituted analogs were particularly photoefficient affording high yields of free cyclohexylamine and the corresponding substituted benzo[*b*]furan as determined by ^{1}H NMR spectroscopy and GC-MS product studies. The photocleavage for this class of substituted carbamates proved particularly clean, affording minimal side products. In contrast, the photochemistry of the *o*-nitrobenzyl class of photobase generators is particularly complex. The parent benzoinyl cyclohexyl carbamate and 2,2-disubstituted α-keto carbamates also formed cyclohexylamine, but the photocleavage was complicated by formation of other photoproducts besides the expected benzo[*b*]furan. Preliminary measurement of the solid state quantum yield for the photogeneration of cyclohexylamine from the cyclohexyl carbamate of 3,3′,5,5′-tetramethoxybenzoin was in the 0.03−0.08 range for exposures in the wavelength range 250 to 370 nm. The variation in quantum yield is consistent with photocleavage proceeding most efficiently via direct n−π* excitation of the carbonyl group at @ 313 nm. In terms of photoefficiency, these materials are comparable to the simple *o*-nitrobenzyl carbamates. However, many of the 3′,5′-dimethoxybenzoinyl carbamates offer a significant advantage in that they are photobleachable. The combination of clean photochemistry and photobleachable absorption makes this class of base photogenerator ideally suited to thick film applications. These materials are currently being evaluated in a number of applications requiring base photogeneration. These include polymer cross-linking and polymer modification reactions of utility in coatings, microlithography, and other imaging applications.

Experimental Procedures

General Procedures. Melting points and boiling points are uncorrected; melting points were recorded on a Gallenkamp melting point instrument. Unless stated otherwise, infrared spectra were obtained as KBr disks using a Nicolet FTIR/44 spectrometer. Ultraviolet−visible spectra were measured in acetonitrile solution or on quartz disks using a Hewlett-Packard 8450A diode array spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a Bruker AF250 spectrometer using tetramethylsilane as internal standard. DSC was performed using a Perkin Elmer cell. TGA was performed on a Perkin Elmer thermobalance. Both thermal techniques used a heating rate of 10 °C/min. GC was performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 5% phenyl methyl silicone fused silica capillary column operating in split injection mode. GC-MS was performed on a Hewlett-Packard GC interfaced to a Hewlett Packard mass-selective detector. Both GC methods used a temperature ramping program involving a 60 °C isothermal for 3.0 min followed by heating at 20 °C/min to 300 °C and holding there at for 10.0 min. Solution photolyses were performed in a Rayonet Photochemical Reactor RPR100 equipped with 16 RPR3500 Å lamps. Microanalyses were performed by Desert Analytics, Tucson, AZ.

Quantum Yield Determination. (a) Sample Preparation. The samples used to determine quantum yields were prepared in the following manner. Poly(methacrylonitrile) (PMAN) (11.0 wt %) was dissolved in nitromethane. The polymer solution was filtered through a 0.45 μm Acrodisc-PTFE filter and diluted with nitromethane to 8.91 wt %. Approximately 5.36 mol % (relative to polymer) of 3,3′,5,5′-tetramethoxybenzoin cyclohexyl carbamate (**2**) was added, and the solution stirred until the carbamate dissolved. The resulting solution was applied to standard silicon, sodium chloride, and quartz substrates with a Headway Research Spin-coater. All films were dried at 90 °C for 15 min and then in vacuo for 12 h. Film thicknesses were measured on a Tencor Alpha Step 200 and were in the range 1.1−1.3 μm.

(b) Evaluation of Quantum Yield. In order to evaluate the quantum yield for the benzoin photocyclization, all the terms in eq 1 must be determined. The starting film concentration of keto carbamate in the film was evaluated from eq 2 as follows. The film weight was found by weighing a blank wafer and then again after coating and drying. Since the weight was very small (@ 1 mg) an average of five wafers was used in this calculation. The weight percent keto carbamate in the film was determined knowing the percent solids distribution in the formulation. The film area was calculated assuming a 1 in. circular wafer.

$$\Phi = \frac{\text{starting film concn (mol·cm}^{-2}) \times \%\ \text{convn}}{\text{radiation flux (einsteins·s}^{-1}\text{·cm}^{-2}) \times \text{time (s)} \times \%\ \text{absorbed}} \quad (1)$$

$$\text{starting film concn (mol·cm}^{-2}) = \frac{\text{total wt of film (g)} \times \text{wt \% keto carbamate}}{\text{area of film (cm}^2) \times \text{molecular wt (g·mol}^{-1})} \quad (2)$$

The changes in the infrared absorbance spectrum of the sample films coated on sodium chloride disks were monitored by quantitative infrared spectroscopy. This was done with use of a Nicolet FTIR/44 spectrometer. The spectra were baseline corrected, and the appropriate peaks were integrated using WinFirst Macros. The photochemical

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rearrangement was followed by monitoring the disappearance of both the keto carbonyl stretch at 1700 cm^{-1} and the carbamate carbonyl stretch at 1716 cm^{-1} in relation to the polymer reference band. The polymer reference band used was the C−H stretch at 3050−2800 cm^{-1}. The ratio (C═O/C−H) of the peak area under the carbonyl absorption and the reference C−H absorption was calculated initially and then again after each successive UV exposure dose. The ratio of the amount of desyl substrate present after irradiation to the amount initially present multiplied by 100 gives the percent desyl substrate remaining after exposure (eq 3).

$$\%\ \text{substrate remaining after exposure} = \frac{\text{final (area C═O band/area C−H band)}}{\text{initial (area C═O band/area C−H band)}} \times \frac{100}{1} \quad (3)$$

From this, the percent conversion caused by each exposure was found by subtraction. For each exposure, two measurements of percent conversion were made on each disk. Conversion values between 5 and 25% were then used directly in the quantum yield calculation. At all exposure wavelengths, plots of percent conversion against exposure time for 3,3′,5,5′-tetramethoxybenzoin cyclohexyl carbamate (**2**) showed a near linear response within this region, thus implying that the inner filter effect was minimal at this extent of reaction.

UV exposure was performed using an OAI exposure tool in conjunction with an Oriel narrow band pass filter at the following exposure wavelengths 254, 313, 336, and 365 nm. The sample coated sodium chloride disks were placed at a distance from the lamp where the light output varied no more than 5% over the exposed region and was in the range 0.20−6.23 mW cm^{-2} depending on the exposure wavelength. The radiation flux at each exposure wavelength was calculated by dividing the light intensity by the energy of one einstein of irradiation at that particular wavelength. Exposure times were obtained directly from an OAI exposure timer.

The percent absorbed is the amount of light absorbed by the sample film at that particular exposure wavelength and was calculated by setting the value for the incident light equal to 100% and subsequently rearranging the Beer−Lambert law. Absorbance values were readily obtained from UV spectra of the sample films. Thus with all the terms in eq 1 having been evaluated, the quantum yield at each exposure wavelength was calculated for several exposure doses. A plot of log quantum yield against the number of quanta absorbed was then used to determine the absolute quantum yield by back extrapolation to zero quanta absorbed. This method of determination corrects for any internal filtering by the benzo[*b*]furan photo byproduct. This procedure was used to calculate the quantum yield for photocyclization of 3,3′,5,5′-tetramethoxybenzoin cyclohexyl carbamate (**2**) at 254, 313, 336, and 365 nm.

Representative Synthesis of Benzoin Carbamates. I. Synthesis of Aryl Substituted α-Keto Carbamates: Preparation of Cyclohexyl Carbamate of 2-(3,5-Dimethoxyphenyl)-2-hydroxy-1-(4-methoxyphenyl)ethanone (4). (a) To a solution of dry, distilled diisopropylamine (7.71 mL, 5.57 g, 55.0 mmol) in anhydrous 1,2-dimethoxyethane (50 mL) at −78 °C under nitrogen was added a solution of n-butyllithium in hexanes (1.6 M, 31.25 mL, 50.0 mmol). The solution was stirred at −78 °C for 1 h and then treated dropwise with a solution of α-(4-methoxyphenyl)-α-(trimethylsiloxy)acetonitrile[47] (11.77 g, 50.0 mmol) in dry 1,2-dimethoxyethane (50 mL). After 1 h at −78 °C, a solution of 3,5-dimethoxybenzaldehyde (9.14 g, 55.0 mmol) in dry 1,2-dimethoxyethane (150 mL) was added, and the reaction was allowed to slowly warm up to 0 °C over 4 h. Once at 0 °C, saturated ammonium chloride (75 mL) was added, and the mixture was stirred for 5 min. Ether (150 mL) was added, and the layers were separated. The organic layer was washed with saturated ammonium chloride (1 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo to give an orange oil (20.21 g). The oil was taken up in tetrahydrofuran (75 mL), and a solution of tetrabutylammonium fluoride in tetrahydrofuran (1 M, 55 mL, 55.0 mmol) was added. The resulting solution was stirred at room temperature under nitrogen for 4 h and concentrated in vacuo, and the residue was partitioned between ether (200 mL) and water (50 mL). The layers were separated, and the organic layer was washed with water (2 × 50 mL) and brine (1 × 50 mL). After drying ($MgSO_4$), removal of the solvent in vacuo gave a yellow oil (18.33 g) which on trituration with methanol gave a solid which was recrystallized from methanol to afford 2-(3,5-dimethoxyphenyl)-2-hydroxy-1-(4-methoxyphenyl)ethanone as a white crystalline solid (8.03 g, 53%), mp 100−101 °C. Anal. Calcd for $C_{17}H_{18}O_5$ (302.31): C, 67.54; H, 6.00. Found: C, 67.74; H 5.93. IR: ν 3366, 1678, 1675, 1601, 1264, 1244, 1207, 1177, 1164, 1087 cm^{-1}. ^{1}H NMR: δ 3.74 (6H, s, Ar(2) 3,5-OCH_3), 3.83 (3H, s, Ar(1) 4-OCH_3), 4.62 (1H, d (J = 5.8 Hz), OH (D_2O exch.)), 5.79 (1H, d (J = 5.8 Hz), 2-CH), 6.36 (1H, t (J_m = 2.2 Hz), Ar(2) 4-H), 6.48 (2H, d (J_m = 2.2 Hz), Ar(2) 2,6-H), 6.87 and 7.93 ppm (each 2H, ABq (J_o = 8.9 Hz), Ar(1) 3,5-H and 2,6-H respectively). ^{13}C NMR: δ 55.23 (q), 55.37 (q), 75.64 (d), 100.20 (d), 105.64 (d), 113.84 (d), 126.14 (s), 131.43 (d), 141.56 (s), 161.11 (s), 164.00 (s), 196.81 (s) ppm.

(b) To a solution of 2-(3,5-dimethoxyphenyl)-2-hydroxy-1-(4-methoxyphenyl)ethanone (2.27 g, 7.5 mmol) in toluene (60 mL) at room temperature under nitrogen was added cyclohexyl isocyanate (1.05 mL, 1.03 g, 8.25 mmol), and the resulting solution was heated at reflux for 48 h. After cooling, the reaction mixture was diluted with ether (100 mL), washed with water (2 × 75 mL) and brine (1 × 50 mL) and dried ($MgSO_4$). Removal of the solvent in vacuo gave the crude product. Trituration with cold toluene gave the crude carbamate as a white solid (2.14 g). Recrystallization from CH_2Cl_2/hexane furnished the desired carbamate (**4**) as a white solid (2.10 g, 66%), mp 105−107 °C. Anal. Calcd for $C_{24}H_{29}NO_6$ (427.58): C, 67.41; H, 6.84; N, 3.28. Found: C, 67.52; H, 6.94; N, 3.31. UV: $\epsilon_{(280)}$18776. IR: ν 3347, 2934, 1713, 1684, 1599, 1513, 1251, 1229, 1172, 1158 cm^{-1}. ^{1}H NMR: δ 1.20−2.05 (10H, m, cyclohexyl $(CH_2)_5$), 3.46 (1H, m, cyclohexyl CH), 3.75 (6H, s, Ar(2) 3,5-OCH_3), 3.83 (3H, s, Ar(1), 4-OCH_3) 4.55 and 4.93 (total 1H, each br d, NH), 6.40 (1H, t (J_m = 2.2 Hz), Ar(2) 4-H), 6.61 (2H, d (J_m = 2.2 Hz), Ar(2) 2,6-H), 6.73 (1H, s, 2-CH), 6.87 and 7.96 ppm (each 2H, ABq (J_o = 7.0 Hz), Ar(1) 3,5-H and 2,6-H respectively). ^{13}C NMR: δ 24.62 (t), 25.32 (t), 33.10 (t), 50.02 (d), 55.29 (q), 55.32 (q), 76.83 (d), 100.94 (d), 106.37 (d), 113.69 (d), 127.52 (s), 131.04 (d), 136.43 (s), 154.54 (s), 160.97 (s), 163.57 (s); 193.02 (s) ppm.

II. Synthesis of 2,2-Disubstituted α-Keto Carbamates: Preparation of Cyclohexyl Carbamate of 2,2-Di-(3,5-dimethoxyphenyl)-2-hydroxy-1-(phenyl)ethanone (7) via 1,1-Di-(3,5-dimethoxyphenyl)-methanone. (a) To a suspension of clean, dry magnesium turnings (3.09 g, 0.127 mol) in dry tetrahydrofuran (20 mL) at room temperature was added a few drops of a solution of 1-chloro-3,5-dimethoxybenzene (19.85 g, 0.115 mol) in dry tetrahydrofuran (100 mL). No visible reaction took place even on adding a few drops of 1,2-dibromoethane. The suspension was then brought to reflux whereupon the addition of a few drops of 1,2-dibromoethane caused a vigorous reaction. The remainder of the aryl chloride solution was added dropwise over 30 min and the solution was heated at reflux overnight. After cooling, the magnesium residues were filtered off under nitrogen and rinsed with tetrahydrofuran (2 × 10 mL). Based on the weight of these residues (0.55 g), the Grignard solution was assumed to contain 0.104 mol of 3,5-dimethoxyphenylmagnesium chloride. To a solution of 3,5-dimethoxybenzonitrile (16.97 g, 0.104 mol) in dry tetrahydrofuran (200 mL) at room temperature under nitrogen was added dropwise a solution of 3,5-dimethoxyphenylmagnesium chloride in tetrahydrofuran (0.104 mol, 65 mL). Once the addition was complete, the solution was heated at reflux for 14 h. After cooling, the tetrahydrofuran was removed in vacuo, and the residue was partitioned between saturated ammonium chloride (150 mL) and ether (200 mL). The layers were separated, and the aqueous phase was extracted with ether (2 × 100 mL). The combined ether extracts was treated with concentrated hydrochloric acid (5 mL) which caused precipitation of a large amount of a fawn solid. The solid was collected by filtration, washed with water (2 × 50 mL) and ether (2 × 50 mL) and dried in vacuo overnight. The solid which amounted to 27.50 g was identified as the ketimine hydrochloride salt. Hydrolysis was achieved by heating a suspension of the salt in a mixture of toluene (100 mL) and 30% sulfuric acid (200 mL) at reflux for 6 h. After cooling, ether (300 mL) was added, and the mixture stirred overnight to dissolve the precipitated ketone. The layers were separated, and the aqueous phase extracted with ether (2 × 75 mL). The combined ether extracts were washed with water (2 × 75 mL) and brine (1 × 75 mL), dried ($MgSO_4$), and concentrated in vacuo to give the crude product as a light brown solid (23.38 g). Recrystallization from ethanol furnished 1,1-di-(3,5-dimethoxyphenyl)-

methanone as a pale yellow solid (20.72 g, 66%), mp 106−108 °C. Anal. Calcd for $C_{17}H_{18}O_5$ (302.31): C, 67.54; H, 6.00. Found: C, 67.52; H, 5.96%. IR: ν 1661, 1600, 1459, 1417, 1345, 1307, 1208, 1201, 1155, 753 cm^{-1}. ^1H NMR: δ 3.83 (12H, s, 3,3′,5,5′-OCH_3), 5.49 (1H, s, CH), 6.67 (2H, t (J_m = 2.3 Hz), 4,4′-H), 6.94 ppm (4H, d (J_m = 2.3 Hz), 2,2′,6,6′-H). ^{13}C NMR: δ 55.45 (q), 104.72 (d), 107.70 (d), 139.23 (s), 160.39 (s), 195.80 (s) ppm.

2,2-Di-(3,5-dimethoxyphenyl)-2-hydroxy-1-(phenyl)ethanone. (b) α-(Phenyl)-α-(trimethylsiloxy)acetonitrile (5.13 g, 25.0 mmol)[48] was lithiated, and the carbanion was treated with 1,1-di-(3,5-dimethoxyphenyl)methanone (7.94 g, 26.3 mmol) in an analogous manner to that described above. The usual workup allowed isolation of 2,2-di-(3,5-dimethoxyphenyl)-2-hydroxy-1-(phenyl)ethanone, TMS ether as an orange gum (13.15 g). This material contained a trace amount of starting material which was recovered after acidolysis and chromatography (vide infra).

For 2,2-di-(3,5-dimethoxyphenyl)-2-hydroxy-1-(phenyl)ethanone, TMS ether, IR: ν 1685, 1596, 1457, 1426, 1312, 1251, 1206, 1157, 1068, 842 cm^{-1}. ^1H NMR: δ 0.24 (9H, s, $OSi(CH_3)_3$), 3.72 (12H, s, 3,3′,5,5′-OCH_3), 6.37 (2H, t (J_m = 2.2 Hz), Ar(2) 4,4′-H), 6.58 (4H, d (J_m = 2.2 Hz), Ar(2) 2,2′,6,6′-H), 7.30 (2H, m approximates to t, Ar(1) 3,5-H), 7.42 (1H, m approximates to t, Ar(1) 4-H), 7.92 ppm (2H, m approximates to d, Ar(1) 2,6-H). ^{13}C NMR: δ 1.28 (q), 55.22 (q), 88.29 (s), 99.47 (d), 106.85 (d), 127.48 (d), 130.21 (d), 131.92 (d), 136.86 (s), 144.87 (s), 160.20 (s), 201.60 (s) ppm.

Acidolysis of the crude 2,2-di-(3,5-dimethoxyphenyl)-2-hydroxy-1-(phenyl)ethanone, TMS ether gave an orange oil (11.95 g) which on flash chromatography furnished the following; elution with 10% EtOAc/90% hexane allowed for the recovery of starting 3,3′,5,5′-tetramethoxybenzophenone as a white solid (1.07 g). Further elution with 25% EtOAc/75% hexane gave a white foam (9.64 g) which was recrystallized from MeOH and then EtOAc/hexane to furnish 2,2-di-(3,5-dimethoxyphenyl)-2-hydroxy-1-(phenyl)ethanone as a fluffy white solid (7.12 g, 77% based on recovered starting ketone), mp 98−99 °C. Anal. Calcd for $C_{24}H_{24}O_6$ (408.43): C, 70.57; H, 5.92. Found: C, 70.76; H, 5.89%. IR: ν 3441, 1676, 1596, 1459, 1426, 1230, 1209, 1159, 1071, 1063 cm^{-1}. ^1H NMR: δ 3.70 (12H, s, 3,3′,5,5′-OCH_3), 4.97 (1H, s, OH (slow D_2O exch.)), 6.42 (2H, t (J_m = 2.2 Hz), both Ar(2) 4,4′-H), 6.58 (4H, d (J_m = 2.2 Hz), Ar(2) 2,2′,6,6′-H), 7.31 (2H, m approximates to t, Ar(1) 3,5-H), 7.47 (1H, m approximates to t, Ar(1) 4-H), 7.73 ppm (2H, m approximates to d, Ar(1) 2,6-H). ^{13}C NMR: δ 55.21 (q), 84.88 (s), 100.08 (d), 106.52 (d), 128.06 (d), 130.62 (d), 132.86 (d), 135.47 (s), 143.72 (s), 160.52 (s), 200.26 (s) ppm.

(c) To a solution of 2,2-di-(3,5-dimethoxyphenyl)-2-hydroxy-1-(phenyl)ethanone (2.04 g, 5.0 mmol) in benzene (50 mL) at room temperature under nitrogen was added stannous 2-ethylhexanoate (0.1 g) followed by cyclohexyl isocyanate (0.70 mL, 0.69 g, 5.49 mmol). After stirring for 24 h, the reaction mixture was preabsorbed onto silica gel (20 g) and purified by flash chromatography using 20% EtOAc/80% hexane as eluant. Subsequent recrystallization from EtOAc/hexane furnished the desired carbamate (**7**) as a white solid (2.67 g, 100%), mp 170−172 °C. Anal. Calcd for $C_{31}H_{35}NO_7$ (533.60): C, 69.77; H, 6.61; N, 2.63. Found: C, 69.64; H, 6.92; N, 2.84%. UV: $\epsilon_{(234)}$23321, $\epsilon_{(278)}$5205. IR: ν 3353, 1726, 1688, 1604, 1597, 1523, 1457, 1209, 1157, 1057 cm^{-1}. ^1H NMR: δ 0.80−2.10 (10H, m, cyclohexyl $(CH_2)_5$), 3.16 (1H, m, cyclohexyl CH), 3.75 (12H, s, Ar(2), 3,3′,5,5′-OCH_3), 4.39 and 4.83 (total 1H, each br d, NH), 6.37 (2H, t (J_m = 2.2 Hz), Ar(2) 4,4′-H), 6.78 (4H, d (J_m = 2.2 Hz), Ar(2) 2,2′,6,6′-H), 7.27 (2H, m approximates to dt, Ar(1) 3,5-H), 7.38 (1H, m approximates to t, Ar(1) 4-H). 7.79 ppm (2H, m approximates to d, Ar(1) 2,6-H). ^{13}C NMR: δ 24.44 (t), 25.22 (t), 32.65 (t), 49.61 (d), 55.22 (q), 87.16 (s), 99.26 (d), 105.57 (d), 127.68 (d), 128.95 (d), 131.30 (d), 136.90 (s,), 142.36 (s), 152.96 (s), 160.24 (s), 195.19 (s) ppm.

Preparative Photolysis. I. Photogeneration of Cyclohexylamine and Preparation of 2-(3,5-Dimethoxyphenyl)-5,7-dimethoxybenzo-[*b*]furan (2a). A Pyrex flask containing a solution of carbamate (**2**) (0.234 g, 0.512 mmol) in dry, degassed acetonitrile (100 mL) was irradiated for 2 h in a Rayonet photolysis chamber fitted with 350 nm lamps. During this time, samples were removed and monitored by GC which indicated that cyclohexylamine was being liberated. After 2 h, TLC confirmed the formation of one major photoproduct along with other trace polar photoproducts. The solvent was removed in vacuo, and the residual oil purified by flash chromatography (10% ethyl acetate/90% hexane) to give 2-(3,5-dimethoxyphenyl)-5,7-dimethoxybenzo[*b*]furan (**2a**) as a white solid (0.137 g, 85%). An analytically pure sample was obtained by recrystallization from ethyl acetate−hexane, mp 106−108 °C (lit.[26] mp 110−111 °C).

Further elution of the column allowed isolation of one minor photoproduct as a yellow oil (0.011 g, 7%). This material was tentatively identified as 1-(3,5-dimethoxyphenyl)-2-(3,5-dimethoxyphenyl)ethanone (**2b**) by ^1H NMR spectroscopy, ^1H NMR: δ 3.77 and 3.83 (each 6H, each s, Ar(1) and Ar(2) 3,3′,5,5′-OCH_3), 4.18 (2H, s, 2-CH_2), 6.37 (1H, t (J_m = 2.2 Hz), Ar(2) 4-H), 6.43 (2H, d (J_m = 2.2 Hz), Ar(2) 2,6-H), 6.65 (1H, t (J_m = 2.2 Hz), Ar(1) 4-H), 7.16 ppm (2H, d (J_m = 2.2 Hz), Ar(1) 2,6-H).

II. Photogeneration of Cyclohexylamine and Preparation of 2-Phenyl-5,7-dimethoxybenzo[*b*]furan (3a). A Pyrex flask containing a solution of carbamate (**3**) (0.196 g, 0.493 mmol) in dry degassed acetonitrile (100 mL) was irradiated for 2 h in a Rayonet photolysis chamber fitted with 350 nm lamps. During this time samples were removed and monitored by GC which indicated that cyclohexylamine was being liberated. After 2 h, TLC confirmed the formation of one major photoproduct along with other trace polar photoproducts. The solvent was removed in vacuo and the residual oil purified by flash chromatography (10% ethyl acetate/90% hexane) to give 2-phenyl-5,7-dimethoxybenzo[*b*]furan (**3a**) as a white solid (0.100 g, 80%). An analytically pure sample was obtained by recrystallization from hexane, mp 68−69 °C (lit.[17] mp 89.1−89.6 °C).

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Supporting Information Available: Copies of figures illustrating UV and IR spectral changes with photolysis for assorted carbamates, (**1**) and (**4**−**6**). Expanded long wavelength photobleaching data on **2**. Illustrations of ^1H NMR spectral changes after 1 h photolysis are available for carbamates (**2**−**4**). Thermal characterization data (DSC and TGA) on carbamates (**2**) and (**3**). Detailed spectroscopic data on benzo[*b*]furans (**2a**) and (**3a**) (17 pages). See any current masthead page for ordering and Internet access instructions.

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