analysis (±5%). Spectral and physical data (^{1}H NMR, IR, bp, mp) were in agreement with the literature data or with those of authentic samples (commercially available or prepared by recognized procedures).

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Base Catalysis in Imaging Materials. 1. Design and Synthesis of Novel Light-Sensitive Urethanes as Photoprecursors of Amines

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The ability to photogenerate active species has led to significant advances in areas as varied as organic synthesis, with the use of photolabile protecting groups, microelectronics with photoresists, and coating technology with photocurable polymers. In imaging techniques such as those used for microlithography, numerous systems have relied on the use of photogenerated acid[1] for their success.[2] In contrast, the use of photogenerated base has essentially not been explored with a few notable exceptions.[3] The reason for this dichotomy is not the lack of applicable chemistry, since base catalysis is widely applicable to numerous reactions but the fact is that photogenerated bases are not readily available.

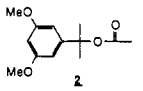
A survey of the literature reveals a few examples of photochemical reactions in which amines are liberated, albeit in low yields, from organic precursors.[4] Typical of these reports are processes in which the amine photoproducts are trapped in solution in their protonated form as they are formed. In the context of systems that require base catalysis, such processes are usually of little practicality as the reactive free amines are not obtained. Most useful perhaps are the classical metal–ammine complexes, which have been used to photogenerate ammonia in a quantum efficient process.[3,5] A significant limitation of such metal–ammine complexes is their inorganic nature, which leads to low solubility in organic systems. Our objectives in this study were to develop efficient organic photoprecursors of simple amines. The design criteria included ease of synthesis, solubility in organic media, and the ability to produce *free* amines by photocleavage using UV irradiation.

Results and Discussion

A simple system, shown in eq 1, is based on the use of a photolabile amino protecting group.

$$R_1R_2N\text{–}PG \xrightarrow{h\nu} R_1R_2NH + PG' \qquad (1)$$

Of the wide range of photosensitive protecting groups available for the amino function,[6] we consider the (α,α-dimethyl-3,5-dimethoxybenzyloxy)carbonyl group (Ddz, **2**) to be the masking group of choice. The Ddz group,[7] as developed for peptide applications,[8] combines the photolability of the (3,5-dimethoxybenzyloxy)carbonyl group[9] with the acid sensitivity of the (α,α-dimethylbenzyloxy)-carbonyl moiety.[10] Removal of the Ddz group from protected amino acid **3** affords the zwitterionic amino acid **4** together with a four-membered photodimerization product, **5**, of 3,5-dimethoxy-1-(2-propenyl)benzene[7] as shown in Scheme I.



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The preferred route[7,8] for the preparation of Ddz-protected amino acids involves the reaction of the carbonyl azide or the pentachlorophenyl mixed carbonate of 3,5-dimethoxy-α,α-dimethylbenzenemethanol with the free amino acid group of the amino acid. In the context of a simple primary amine protected as in structure **6** (Scheme II), this approach amounts to disconnection A. We favor the alternate disconnection route B, which involves readily available isocyanates **7** and tertiary alcohol **8**. While the direct addition of isocyanates to tertiary alcohols is usually inefficient,[11] the reaction proceeds more satisfactorily in the presence of a lithium alkoxide catalyst.[12] The required alcohol **8** is readily prepared by a simple Grignard reaction from the commercially available methyl 3,5-dimethoxybenzoate.[7] Isocyanates were chosen for their ultimate ability to afford photoactive carbamates capable of liberating strongly basic amines upon irradiation as shown in Scheme III for compound **9**.

In contrast to the uncatalyzed reaction, which proved inefficient, the lithium alkoxide catalyzed addition of tertiary alcohol **8** to cyclohexyl isocyanate afforded a high yield (80%) of a white crystalline solid, which proved to

(1) Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307. Crivello, J. V., *Adv. Polym. Sci.* **1984**, *62*, 1. Crivello, J. V. *Polym. Mat. Sci. Eng.* **1989**, *61*, 62.

(2) Fréchet, J. M. J.; Bouchard, F.; Eichler, E.; Houlihan, F. M.; Iizawa, T.; Kryczka, B.; Willson, C. G. *Polymer J.* **1987**, *19*, 31. Willson, C. G.; Ito, H.; Fréchet, J. M. J.; Tessier, T. G.; Houlihan, F. M. *J. Electrochem. Soc.* **1986**, *133*, 181. Crivello, J. V.; Conlon, D. A.; Lee, J. L. *Polym. Mat. Sci. Eng.* **1989**, *61*, 422. Houlihan, F. M.; Reichmanis, E.; Thompson, L. F.; Tarascon, R. G. In *Polymers for Microlithography*; E., Reichmanis, S. A., MacDonald, T., Iwayanagi, Ed.; ACS Symposium Series 412; American Chemical Society: Washington DC, 1989; Chapter 3, p 39.

(3) Kutal, C.; Willson, C. G. *J. Electrochem. Soc.* **1987**, *134*, 2280. Kutal, C.; Weit, S. K.; Willson, C. G. *Proc. Polym. Mat. Sci. Eng.* **1989**, *61*, 195.

(4) Inoue, H.; Hiroshima, Y.; Miyazaki, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 664. Inoue, H.; Hiroshima, Y.; Sakai, T.; Sakurai, T.; Fukuda, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2829. Birch, D.; Coyle, J. D.; Hill, R. R.; Jeffs, G. E.; Randall, D. *J. Chem. Soc. Chem. Commun.* **1984**, 796. Mandl, I.; McLaren, A. D. *J. Am. Chem. Soc.* **1951**, *73*, 1826. Brinton, R. K. *J. Am. Chem. Soc.* **1955**, *77*, 842. Horne, D. G.; Norrish, R. G. W. *Proc. R. Soc. London, Ser. A* **1970**, *315*, 301. Specht, D. P.; Williams, J. L. R.; Chen, T. H.; Farid, S. *J. Chem. Soc. Chem. Commun.* **1975**, 705. Walsh, T. D.; Long, R. C. *J. Am. Chem. Soc.* **1967**, *89*, 3943. Furrer, H. *Tetrahedron Lett.* **1974**, 2953. Katritzky, A. R.; Chapman, A. V.; Cook, M. J. Millet, G. H. *J. Chem. Soc. Chem. Commun.* **1979**, 395.

(5) Balzani, S. V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: 1970; p 197. Endicott, J. F. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D. Eds.; Wiley-Interscience: New York, 1975; p 81.

(6) Pillai, V. N. R. *Synthesis* **1980**, 1. Amit, B.; Zehavi, U.; Patchornik, A. *Isr. J. Chem.* **1974**, *12*, 103. Zehavi, U. *Adv. Carbohydr. Chem. Biochem.* **1988**, *46*, 179.

(7) Birr, C.; Lochinger, W.; Stahnke, G.; Lang, P. *Liebigs Ann. Chem.* **1972**, *763*, 162.

(8) Birr, C. *Liebigs Ann. Chem.* **1973**, 1652. Birr, C. *Peptides, Proc. 12th Eur. Pept. Symp. 1972*; Hanson, H., Jakubke, H.-D. Eds.; North Holland Publishing Company: Amsterdam, 1973, p 72. Birr, C. *Peptides Proc. 13th Eur. Pept. Symp.* **1973**; Wolman, Y., Ed.; Halsted Press: New York, 1974; p 117. Birr, C.; Flor, F.; Fleckenstein, P.; Wieland, T. *Peptides, Proc. 11th Eur. Pept. Symp. 1971*; Nesvadba, H., Ed.; North Holland Publishing Company: Amsterdam, 1972; p 175.

(9) Chamberlin, J. W. *J. Org. Chem.* **1966**, *31*, 1658.

(10) Sieber, P.; Iselin, B. *Helv. Chim. Acta* **1968**, *51*, 614.

(11) Davis, T. L.; Farnum, J. McC. *J. Am. Chem. Soc.* **1934**, *56*, 883. Neuberg, C.; Kansky, E. *Biochem. Z.* **1909**, *20*, 446.

(12) Bailey, W. J.; Griffith, J. R. *J. Org. Chem.* **1978**, *43*, 2690.

(13) Wendisch, D.; Reiff, H.; Dieterich, D. *Angew. Makromol. Chem.* **1986**, *141*, 173.

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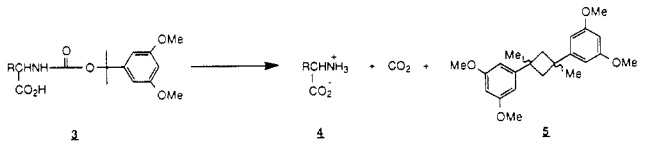
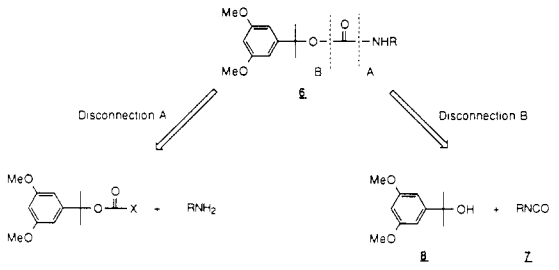
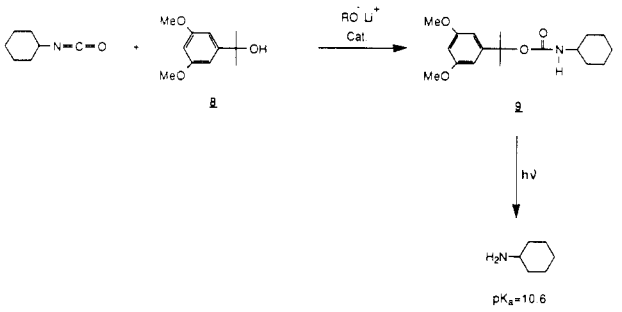
Scheme I



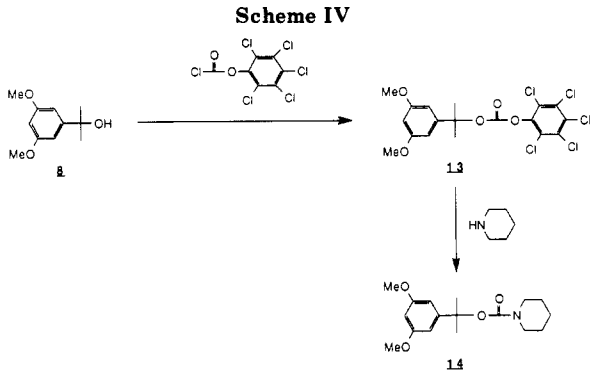
Scheme II



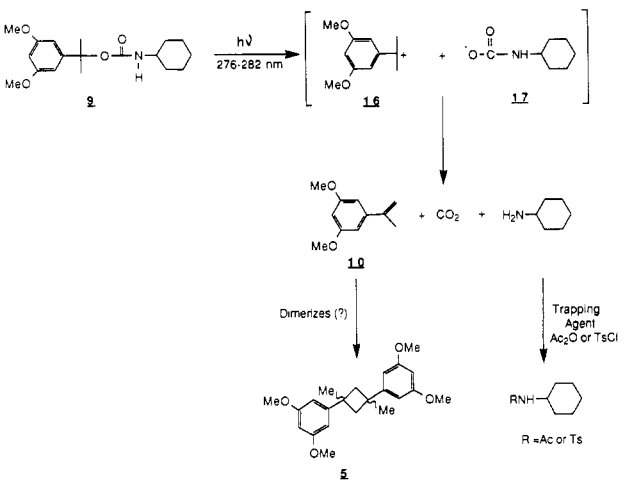
Scheme III



Scheme IV

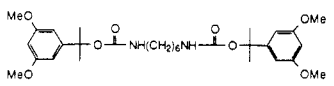


Scheme V

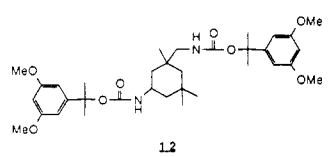


be the expected carbamate **9** as confirmed by ^1H and ^{13}C NMR and IR spectroscopy. Mass spectrometry further confirmed the structure of the carbamate **9** by displaying the appropriate weak molecular ion at m/z 321.1913 ($M^+ = C_{18}H_{27}NO_4$, requires m/z 321.1940). The observed fragmentation of this molecular ion leads to cyclohexylamine and 3,5-dimethoxy-α-methylstyrene (**10**).

The synthetic methodology used to prepare urethane **9** was extended to the preparation of bis-Ddz carbamates, which, on UV exposure, should liberate diamines. The 1,6-hexanedicarbamate **11** was also prepared by the direct addition of alcohol **8** to 1,6-diisocyanatohexane. In this case, the use of methyllithium rather than lithium metal to prepare the lithium alkoxide allowed for an improved yield of 52% of **11**. The isophorone diamine bis-carbamate **12** was also obtained by using this procedure as a complex mixture from which the dicarbamate having trans[13] stereochemistry was isolated in pure form by repeated flash chromatography and recrystallization, hence the reduced yield of 35%.

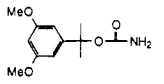


11



12

Unfortunately, Ddz-containing carbamates capable of photogenerating secondary amines are not available by using this direct addition protocol, and a more involved process (Scheme IV), analogous to that used previously for amino acids, was required. Activation[7] of alcohol **8** as the pentachlorophenyl mixed carbonate **13** and subsequent reaction of **13** with piperidine afforded the desired carbamate **14** in 49% overall yield for the two-step process. The same procedure was also used to obtain carbamate **15**, which acts as a photoprecursor of ammonia.



15

Photogeneration of Amines. Carbamate **9** exhibits the typical UV absorption of the Ddz chromophore at 276 and 282 nm.[7,8] These UV absorption characteristics are favorable in terms of creating a base photogenerator useful for deep-UV microlithography (Scheme V).

The photodecomposition pathway of carbamate **9** was first established in solution. Irradiation of a 10 mM solution of **9** resulted in complete deprotection to form two main photoproducts. The disappearance of the starting carbamate was monitored by TLC while the appearance of the photoproducts was more readily monitored by GC. Co-injection with cyclohexylamine allowed the tentative assignment of the first photoproduct as cyclohexylamine. Isolation of the volatile cyclohexylamine was facilitated by the in situ preparation of its *N*-acetyl derivative using acetic anhydride as a trapping agent. Interestingly, the second photoproduct, which, based on the reported mode of Ddz cleavage,[7,8] was expected to be the photodimer **5**, actually proved to be 3,5-dimethoxy-α-methylstyrene (**10**).

Overall, the photocleavage of active carbamate **9** proceeds as shown in Scheme V, with initial heterolytic cleavage of the benzyloxy bond to afford the fragments **16** and **17**, which, on subsequent elimination liberate the styrenic product **10**, CO_2, and free cyclohexylamine.

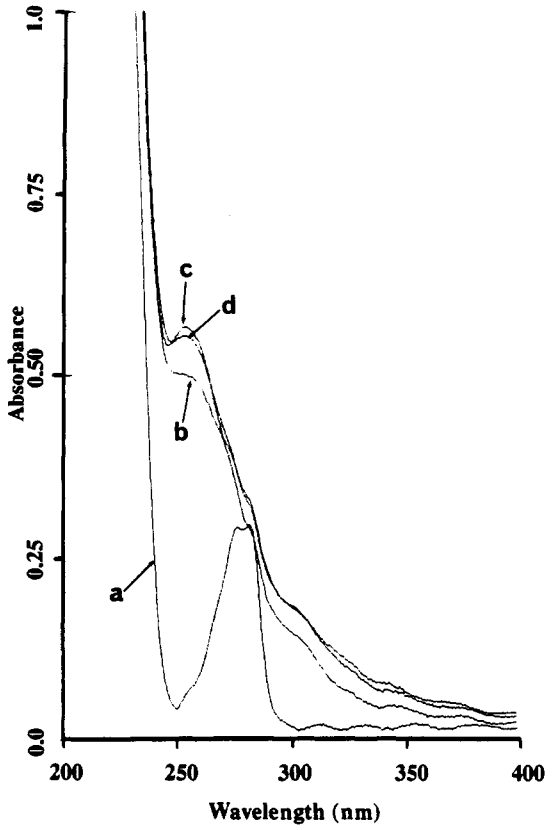


Figure 1. UV spectra of 1-μm thick film of poly(methyl methacrylate) containing 10 mol % of carbamate **9** with increasing UV exposure dose: (a) prior to irradiation, (b) after 110 mJ/cm^2 dose, (c) after 220 mJ/cm^2 dose, (d) after 330 mJ/cm^2 dose.

This mode of photocleavage of carbamate **9** was further confirmed by another photolysis-trapping experiment in which the photogenerated cyclohexylamine was trapped as its *N*-toluenesulfonamide derivative. Finally, a GC-MS study of the photodecomposition of **9** allowed observation of the appropriate molecular ions and subsequent decay patterns for both free cyclohexylamine and 3,5-dimethoxy-α-methylstyrene (**10**).

The solid-state photosensitivity of **9** was explored by monitoring the UV spectrum of a 1-μm thick film of PMMA containing 10 mol % of **9** spin-coated onto a quartz substrate, with increasing exposure to a UV source. From Figure 1, it is apparent that the characteristic Ddz absorptions at 276 and 282 nm disappear as the carbamate is photocleaved, while the absorption at 252 nm increases due to formation of 3,5-dimethoxy-α-methylstyrene (**10**), with concomitant liberation of the desired cyclohexylamine. As expected, similar as well as complementary experiments with the other amine photoprecursors **11**, **12**, **14**, and **15** suggest that they all undergo the same photocleavage reaction in solution and in the solid state.

Thermal Stability. For Ddz-protected amines to be potentially useful in the formulation of resist materials or imaging systems they must be thermally stable under the standard processing conditions that include heating to temperatures as high as 150 °C. This proved to be the case with the cyclohexylamine photogenerator **9** as confirmed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). the DSC curve of carbamate **9** shows two transitions; the first, at 90 °C, corresponds to the melting point while the latter, near 200 °C, is the decomposition temperature. The decomposition temperature was confirmed by TGA, which showed a quantitative weight loss occurring between 200 and 250 °C. Table I records the melting and decomposition temperatures of the various photoactive carbamates.

Table I. Melting Points and Decomposition Temperatures of the Photoactive Carbamates

structure	mp (°C)	dec[a] temp (°C)
9	90–91	211
11	103–5	206
12	149–50	204
14	*b*	193
15	95–97	201

[a] Determined by thermogravimetric analysis as the point of 5% weight loss. [b] Liquid with boiling point 200 °C at 0.01 mmHg.

Conclusions

A novel approach toward the photogeneration of base has been investigated. The principle of using the photolabile Ddz moiety to mask amines affords an organic source of photogenerated amine. The Ddz group is photocleaved cleanly in both the solid state and in solution. This makes it particularly attractive for use in applications requiring photogenerated base. The practical potential of such a system is further indicated by the mid-UV absorption characteristics of the photocleavage and the thermal stability of the Ddz-based carbamates.

Experimental Procedure

General Procedures. Melting points and boiling points are uncorrected. IR spectra (KBr pellets) were obtained on a Nicolet FTIR/44 spectrometer. UV–vis spectra were measured from THF solution using a Nicolet 9430 spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a Bruker AF300 spectrometer using TMS as internal standard. Mass spectra were obtained from a Kratos MS890 high resolution spectrometer. DSC (Mettler DSC30) and TGA (Mettler TG50 Thermobalance) were performed at a heating rate of 10 °C/min. GC was performed on a Nicolet 9630 gas chromatograph with a 5% phenylmethyl silicone fused silica capillary column operating in a split injection mode. GC-MS was performed on a HP 5890-II chromatograph with HP 5970B mass selective detector. Film thicknesses were measured were obtained on a Tencor alpha-step. Solid-state photolyses were performed by using an OAI exposure tool. Solution photolysis in quartz glassware used a Canrad-Hanovia 450-W mercury source. Microanalyses were performed by M.H.W. Laboratories, Phoenix, AZ.

Preparation of *N*-[[1-(3,5-Dimethoxyphenyl)-1-methylethoxy]carbonyl]cyclohexylamine (9). A solution of alcohol[7] (**8**) (1.962 g, 10.0 mmol) in ether (50 mL) at 22 °C under N_2 was treated with lithium (0.01 g, 1.5 mmol), then heated at reflux for 2 h, cooled to room temperature, and treated dropwise with cyclohexyl isocyanate (1.28 mL, 1.252 g, 10.0 mmol) in ether (10 mL). After being refluxed for 14 h, the cooled mixture was treated with methanol (1 mL)–water (5 mL). The organic layer was washed with H_2O and brine and then dried over $MgSO_4$. After evaporation, flash chromatography (15% EtOAc/85% hexane) and recrystallization (hexane) afforded the desired carbamate **9** as a white crystalline solid (2.583 g, 80%): mp 90–91 °C.

Anal. Calcd for $C_{18}H_{27}NO_4$ (321.41): C, 67.26, H, 8.47, N, 4.36. Found: C, 67.18, H, 8.52, N, 4.48.

IR: 3326 (s, N–H), 1714 and 1689 (s, C=O), 1612 and 1590 (m, C-C), 1531 cm^{-1} (s, N-H). ^{1}H NMR: δ (ppm) 6.51 [2 H, d (J_m = 2 Hz)], 6.34 [1 H, t (J_m = 2 Hz)], 4.63 [1 H, d (J = 8 Hz)], 3.78 [3 H, s], 3.44–3.34 [1 H, br, m], 2.07–1.56 [10 H, m], 1.35–1.04 [6 H, m]. ^{13}C NMR: δ (ppm) 160.68, 154.39, 149.43, 103.03, 98.43, 80.43, 55.21, 49.57, 33.55, 29.02, 25.55, 24.84. UV: λ_{max} 282 (ϵ = 2118) and 276 nm (ϵ = 2123). MS: found m/z 321.1913 (M$^+$ = $C_{18}H_{27}NO_4$), 196.1072 ($C_{11}H_{16}O_3$), 178.0991 ($C_{11}H_{14}O_2$), 99.1044 ($C_6H_{13}N$).

Preparation of *N*,*N*′-Bis[[1-(3,5-dimethoxyphenyl)-1-methylethoxy]carbonyl]hexane-1,6-diamine (11). A solution of alcohol **8** (2.944 g, 15.0 mmol) in ether (20 mL) at 22 °C under N_2 was treated with methyllithium (1.4 M in ether, 0.54 mL, 0.75 mmol), stirred for 5 h, and then treated dropwise with 1,6-di-

isocyanatohexane (1.21 mL, 1.262 g, 7.5 mmol) in dry ether (10 mL), which caused a vigorous reaction. The reaction mixture was refluxed for 10 h, cooled, and then concentrated. The residue was dissolved in $CHCl_3$, washed with water and brine, then dried ($MgSO_4$), evaporated, and purified by flash chromatography (35/65 EtOAc/hexane). Some unreacted 8 (0.418 g, 14%) was recovered, and the desired product 11 was recrystallized from EtOAc–hexane (1.867 g, 52%), mp 103–105 °C.

Anal. Calcd for $C_{30}H_{44}N_2O_8$ (560.67): C, 64.26, H, 7.91, N, 5.00. Found: C, 64.65, H, 7.84, N, 4.78.

IR: 3300 (s, N–H), 1717 and 1693 (s, C=O), 1609, 1601 (s, C–C), 1532 cm^{-1} (s, N–H). ^1H NMR: δ (ppm) 6.51 [4 H, d (J_m = 2 Hz)], 6.34 [2 H, t (J_m = 2 Hz)], 4.75 [2 H, br t (J = 5 Hz)], 3.78 [12 H, s], 3.10–3.01 [4 H, m], 1.72 [12 H s], 1.55–1.25 [8 H, m]. ^{13}C NMR: δ (ppm) 166.55, 155.14, 149.28, 102.95, 98.10, 80.30, 55.18, 40.32, 29.93, 29.01, 26.14. UV: λ_{max} 282 (ϵ = 4092) and 276 nm (ϵ = 4135).

Preparation of the Trans Bis-Ddz Derivative of Isophorone Diisocyanate 12. A solution of 8 (2.944 g, 15.0 mmol) in ether (40 mL) at room temperature under N_2 was treated with methyllithium (1.4 M in ether, 1.07 mL, 1.5 mmol), refluxed for 2 h, cooled, and then treated dropwise with isophorone diisocyanate (mixture of stereoisomers, 1.59 mL, 1.667 g, 7.5 mmol) in ether. After 14 h of reflux, workup as above followed by flash chromatography (hexane/EtOAc 3:1) and recrystallization (acetone–cyclohexane) afforded the trans-bis-carbamate **12** (trans structure assigned per ref 13) as a white solid (1.662 g, 35%): mp 149–150 °C.

Anal. Calcd for $C_{34}H_{50}N_2O_8$ (614.76): C, 66.42, H, 8.20, N, 4.56. Found: C, 66.42, H, 8.32, N, 4.65.

IR: 3700–3100 (m, br N–H), 1711 (s, C=O), 1599 cm^{-1} (s, C–C). ^1H NMR: δ (ppm) 6.50 [4 H, overlapping d], 6.34 [2 H, overlapping t], 4.80 [1 H, t (J = 6 Hz)], 4.57 [1 H, d (J = 6 Hz)], 3.79 and 3.78 [each 6 H, each s], 3.75–3.69 [1 H, m], 2.92–2.72 [2 H, complex m], 1.78–1.56 [14 H, m], 1.17–0.75 [13 H]. ^{13}C NMR: δ (ppm) 160.61, 155.41, 154.37, 149.35, 149.22, 103.12, 102.82, 98.33, 97.98, 80.44, 80.35, 55.25, 55.22, 54.21, 46.96, 46.43, 44.16, 41.59, 36.45, 35.00, 31.82, 29.13, 28.53, 27.57, 23.48. UV: λ_{max} 282 (ϵ = 4057) and 276 nm (ϵ = 4092).

Preparation of *N*-[[1-(3,5-Dimethoxyphenyl)-1-methylethoxy]carbonyl]piperidine (14). To a solution of the pentachlorophenyl carbonate ester[7] of 3,5-dimethoxy-α,α-dimethylbenzenemethanol (**13**, 3.288 g, 10.0 mmol) in THF at room temperature under N_2 was added dropwise a solution of piperidine (1.98 mL, 1.703 g, 20.0 mmol) in THF (10 mL) over 15 min. After 12 h of stirring followed by 2 h of reflux, the mixture was worked up as above to afford a yellow oil (2.50 g) which, after flash chromatography (15/85 EtOAc/hexane) and Kugelrohr distillation afforded carbamate **14** as a colorless viscous oil (1.816 g, 59%): bp 200 °C at 0.01 mmHg.

Anal. Calcd for $C_{17}H_{25}NO_4$ (307.38): C, 66.42, H, 8.20, N, 4.56. Found: C, 66.27, H, 8.44, N, 4.63.

IR: 1705 (C=O), 1598 cm^{-1} (s, C–C). UV: λ_{max} 282 (ϵ = 2572) and 276 nm (ϵ = 2578). ^1H NMR: δ (ppm) 6.50 [2 H, d (J_m = 2 Hz)], 6.34 [1 H, t (J_m = 2 Hz)], 3.78 [6 H, s], 3.55–3.25 [4 H, br s], 1.75 [6 H, s], 1.70–1.50 [6 H, br m]. ^{13}C NMR: δ (ppm) 160.55, 154.08, 149.54, 102.88, 99.13, 80.48, 55.16, 44.97, 29.10, 25.90, 24.47.

Preparation of [[1-(3,5-Dimethoxyphenyl)-1-methylethoxy]carbonyl]amine (15). A large excess of ammonia was condensed into a solution of the pentachlorophenyl carbonate ester of 3,5-dimethoxy-α,α-dimethylbenzenemethanol (**13**) (2.440 g, 5.0 mmol) in THF (50 mL) at −78 °C. After being stirred for 4 h, the mixture was allowed to warm to room temperature overnight. Workup as above followed by flash chromatography (50/50 EtOAc/hexane) and recrystallization (ether–hexane) afforded carbamate **15** as colorless crystals (0.959 g, 80%): mp 95–97 °C.

Anal. Calcd for $C_{12}H_{17}NO_4$ (239.27): C, 60.23, H, 7.16, N, 5.83. Found: C, 60.42, H, 7.32, N, 6.01.

IR: 3474 and 3441 (m, primary N–H), 1701 (s, C=O), 1609 (m, C–C), 1589 cm^{-1} (m, N–H). ^1H NMR: δ (ppm) 6.52 [2 H, d (J_m = 2 Hz)], 6.35 [1 H, t (J_m = 2 Hz)], 4.70 [2 H, br s], 3.79 [6 H, s], 1.73 ppm [6 H, s]. UV: λ_{max} 282 (ϵ = 1906) and 276 nm (ϵ = 1909). ^{13}C NMR: δ (ppm) 160.60, 155.34, 148.68, 102.91, 98.15, 80.91, 55.22, 28.86.

Photolysis of 9: Photogeneration of Cyclohexylamine. A solution of carbamate **9** (0.804 g, 2.50 mmol) in dry, degassed THF (250 mL) was irradiated for 24 h at room temperature by using a 450-W medium pressure mercury lamp. At this stage TLC indicated that the photolysis was complete, and GC implied that two principal photoproducts were formed. Co-injection of the reaction mixture with cyclohexylamine revealed the component with the shortest retention time to be cyclohexylamine. Because of the volatility and polarity of cyclohexylamine, the following derivatization protocol to *N*-acetylcyclohexylamine was employed. The photolysate was concentrated to a volume of 15 mL at atmospheric pressure by using an efficient fractionating column and was subsequently treated with a large excess of acetic anhydride. After heating at reflux for 16 h, GC indicated the absence of cyclohexylamine and the presence of two components. Co-injection identified the component with the shortest retention time as now being *N*-acetylcyclohexylamine. The other photoproduct remained unchanged during this acetylation process. After removal of the solvent in vacuo, the residue was taken up in ether (25 mL) and washed with water (2 × 5 mL) and brine (1 × 5 mL). The solution was dried over $MgSO_4$ and concentrated under reduced pressure to give a brown oil (1.34 g), which proved to be a two-component mixture. The original photoproduct was isolated as a colorless oil (25 mg) by flash chromatography using 10% EtOAc/90% hexane as eluant. This material was identified spectroscopically as 3,5-dimethoxy-α-methylstyrene (**10**). Further elution with 10/90 MeOH/EtOAc afforded *N*-acetylcyclohexylamine as a light brown solid (0.132 g). A GC-MS study of the photolysis products before acetylation confirmed the formation of cyclohexylamine (M^+ = 99) and 3,5-dimethoxy-α-methylstyrene (**10**) (M^+ = 178).

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