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The photogeneration of organic dimethoxybenzyl carbamates is descr are prepared easily through react addition of isocyanates to α, α -dimet through the use of active ester chem mates that can be used to generate p as diamines has been tested succes upon exposure of the carbamates to b inary tests indicate that photoac nitrobenzyl groups are also readily	amines from α, α -dimethyl-3,5- tibed. The photoactive carbamates tions involving the Li catalyzed thyl-3,5-dimethoxybenzyl alcohol or mistry. A variety of active carba- primary or secondary amines as well sfully. Free amines are liberated JV radiation below 300 nm. Prelim- tive carbamates incorporating o- y obtainable from isocyanates.	
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Photogenerated Amines and Diamines: Novel Curing Systems for Thin Film Coatings

by

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PHOTOGENERATED AMINES AND DIAMINES: NOVEL CURING SYSTEMS FOR THIN FILM COATINGS

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The photogeneration of acid within solid matrices such as thin films or coatings has led to significant developments in the areas of photocurable coatings [1], imaging materials [2], and resists for microlithography [3]. In these systems, the ability to photogenerate acid *in situ* within a solid matrix is key to subsequent steps that may involve polymerization [1], depolymerization [4], catalyzed thermolysis [3] or electrophilic aromatic substitution processes [5].

In view of the wealth of chemistry that may be promoted or catalyzed by base and is therefore applicable to coating, imaging, and resist chemistry, it is desirable to prepare efficient organic photo-precursors of amines that may be used efficiently in the solid state.

We have developed recently [6] a family of carbamates based on α, α dimethyl-3,5-dimethoxybenzyl (Ddz) chemistry that can be used to generate amines by exposure to UV light below 300nm. This report describes some of these carbamates as well as another family of active compounds that may also be used with longer wavelength radiation and possess extremely high quantum efficiencies in the solid state.

1. Chemistry of a, a-dimethyl-3,5-dimethoxybeazyl varbasastes.

The procedure used for the preparation of α, α -dimethyl-3,5-dimethoxybenzyl (Ddz) carbamates are described elsewhere [6]. Typically the most convenient route for the Ddz protection of primary amines or diamines involves the reaction of the corresponding isocyanates with α, α -dimethyl-3,5-dimethoxybenzyl alcohol in the presence of a suitable catalyst. For example, Scheme 1 shows the preparation c^{-1} be Ddz derivative 1 of 1,6-diaminohexane. A slightly different rout, available [6] for use with secondary amines.



The photogeneration of free amines from their Ddz carbamates was studied both in solution and in the solid-state. In both cases the photocleavage proceeds with liberation of the free amine, carbon dioxide and 3,5-dimethoxy- α -methyl styrene as shown in Scheme 2 for the photoprecursor of 1,6-hexanediamine. Though alternate mechanistic pathways are possible, it is believed that the photocleavage proceeds by initial heterolytic cleavage of the benzylic C-O bond of the Ddz carbamate.



This is facilitated by the strong electron donating effect of the methoxy substituents in the photochemically excited state. The solid state reaction was explored by monitoring the behavior of the photoactive carbamates within poly(methyl methacrylate) and poly(methacrylonitrile) matrices. Quantum yield measurements performed on such films spin-coated on quartz (UV measurements for PMMA films) and on NaCl windows (IR measurements for PMAN films) showed that the desired photocleavage and production of free amine occurred with a reasonably high efficiency as a value of 0.10 was obtained for the quantum yield in the solid-state

reaction. Figure 1 shows the change in carbonyl absorption of the α, α dimethyl-3,5-dimethoxybenzyloxycarbamoylcyclohexane versus time upon UV exposure at 280nm.



Figure 2 shows a plot of log quantum yield versus number of quanta absorbed for the same α , α -dimethyl-3,5-dimethoxybenzyloxycarbamoyl-cyclohexane upon exposure at 280nm; as shown on this plot, extrapolation to zero results in a quantum yield value of 0.10 for this system.



The photolabile 2-nitrobenzyl group has been used previously as a protecting group for alcohols, amino acids, and peptides. While earlier procedures have involved the use of 2-nitrobenzyl chloroformate in the protection step, and indeed we have used this reagent to prepare 2, we have found that it is unsuitable for the protection of diamines such as hexane-1,6-diamine as decarboxylation occurs and the product that is isolated is the tertiary amine. In contrast, the direct addition of an alcohol to an isocyanate (Scheme 3) catalyzed by dibutyl tin dilaurate is very effective and can be used for example to prepare bis-carbamate 3.



Both $\underline{2}$ and $\underline{3}$ are photoactive and liberate cyclohexylamine and hexane-1, 6-diamine respectively upon exposure to UV light below 400nm as shown in Scheme 4.



SCHEME 4.

The solid-state quantum efficiency of 2 can be determined by coating NaCl plates with a film of poly(methyl methacrylate) containing 7-10 mole % of 2 and monitoring the disappearance of the asymmetric N-O



stretch by IR spectroscopy with increasing UV exposure dose. The deprotection reaction s_3n easily be sarried to completion but typical quantum yield measurements are best performed at conversions between 5 and 25%. Typical quantum efficiencies for the photodecomposition of 2 with liberation of cyclohexylamine are of the order of 0.13 at 254nm, a value which was calibrated by parallel solid-state measurements with the known [7] actinometer, 2-nitrobenzaldehyde.

In an attempt to increase this quantum yield, the 2,6-dinitrobenzyl group was substituted for the 2-nitrobenzyl group in the preparation of photoactive carbamate $\underline{4}$. The best procedure for the preparation of $\underline{4}$ involved the reaction of 2,6-dinitrobenzyl alcohol with cyclohexyl isocyanate in the presence of a catalytic amount of methyl lithium. Carbamate $\underline{4}$ obtained in 78% yield was found to be remarkably active when irradiated with UV light below 400nm. For example its solid-state quantum efficiency at 254nm is 0.62 when exposed within a film of poly(methyl methacrylate) [8].



Earlier work on the use of similar 2-nitrobenzyl-based protecting groups in amino-acid chemistry had suggested that significant recombination of the liberated nitro-benzaldehyde with the newly faced amino-groups of the deprotected amino-acid was taking place [9]. This process, if prevalent, could be troublesome even though the resulting N-alkylimines would readily hydrolyze to free amines in the presence of water.

In an attempt to determine whether or not this process was significant with carbamates such as 2-4, their photodecomposition in solution was monitored by GC-MS. These studies failed to show the presence of an imine such as 5 while free cyclohexylamine was observed and remained in solution even upon prolonged standing in the presence of other photoproducts.



Nevertheless a third type of carbamate in which the photo by-product would be a nitroso ketone rather than a nitrosoaldehyde was also investigated as this by-product would be even less prone to spontaneous recombination with the liberated amine. Carbamate $\underline{6}$ was obtained in 71% yield by the lithium alkoxide catalyzed reaction of cyclohexyl isocyanate with α -methyl-2-nitro benzenemethanol. Similarly, bis-carbamate $\underline{7}$ was obtained in 69% yield by the same reaction with 1,6-diisocyanatohexane.



Solid-state photolysis of $\underline{6}$ in a poly(methyl methacrylate) matrix showed a quantum efficiency of 0.11, while GC-MS monitoring of its photolysis in solution showed no evidence of imine formation while free cyclohexy-lamine was observed together with other photo-by-products.

The photoactive carbamates described in this study appear to be efficient photo precursors of free amines [6, 8]. The very high quantum efficiency obtained in the photolysis of $\underline{4}$ is of particular interest. Additional experiments involvilving the photocuring of epoxy resins with diamines liberated from $\underline{3}$ or $\underline{7}$ have further confirmed the usefulness of this new family of amine photo-precursors. These experiments as well as other 'developments involving the use of our photogeneratod amines will be described elsewhere.

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