Photoactive Materials Applicable to Imaging Systems

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Whereas many photoinitiator systems produce an acid to effect polymerization or a change in substrate acidity, few systems are available for reliable, high yielding formation of a base. Nitro-substituted urethanes **1a–i** have been shown to afford excellent yields of primary or secondary alkyl or aryl amines on photolysis in the near UV and, more importantly, in the visible region, appropriate for exposure with standard light sources.

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Introduction

Photogeneration of active species has proved extremely important in many areas and photolabile protecting groups have been used widely in organic and bio-organic synthesis.[1] Photocurable polymers have found many applications in coating technology[2] and photoresists are important in fabrication of microelectronic devices.[3] Although some such applications involve very short wavelength ultraviolet irradiation or even electron beams, most commercial systems use ultraviolet or visible light sources because of their ease of use and low cost.

In lithography, compounds that produce radicals and/or acids on photolysis have been used extensively as photoinitiators in positive and negative imaging systems. Thus, irradiation with light is used to effect polymer degradation,[4] polymer formation,[5] or polymer side-chain modification.[2] In situ generation of acid is used as a means of inducing polymerization of monomers or oligomers or to effect cross-linking and both of these processes normally lead to less soluble materials. Despite the possibilities for application of base catalysis, the use of photogenerated bases in imaging systems has attracted little attention. In most photochemical reactions that liberate a base (usually an amine), it is trapped in solution in its largely neutral protonated form so that such processes are of little utility with systems that require base catalysis. Major exceptions lie in deep-UV irradiation of transition metal-amine complexes with negative photoresist systems,[3] which photogenerate ammonia in a quantum efficient process, and

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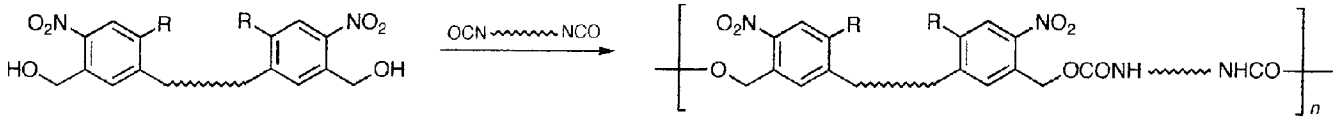
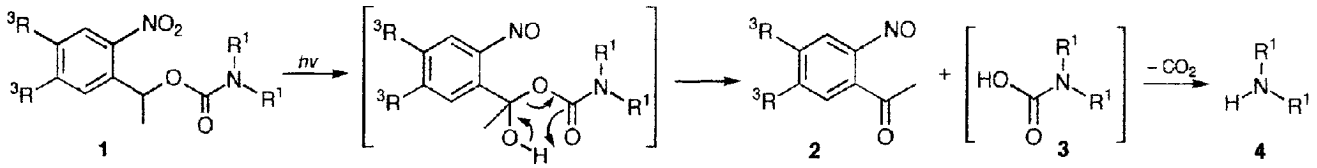


Reaction 1.



Scheme 1.

short wavelength irradiation of α,α-dimethyl-3,5-dimethoxybenzyloxy carboxamides, which yield amines.[6] The release of aliphatic surfactant amines from substituted N-benzyl-N-alkylamine precursors by deep-UV irradiation has also been reported.[7] However, compared with acid-release systems, few general base-release agents are useful for short- and long-wavelength lithographic applications.

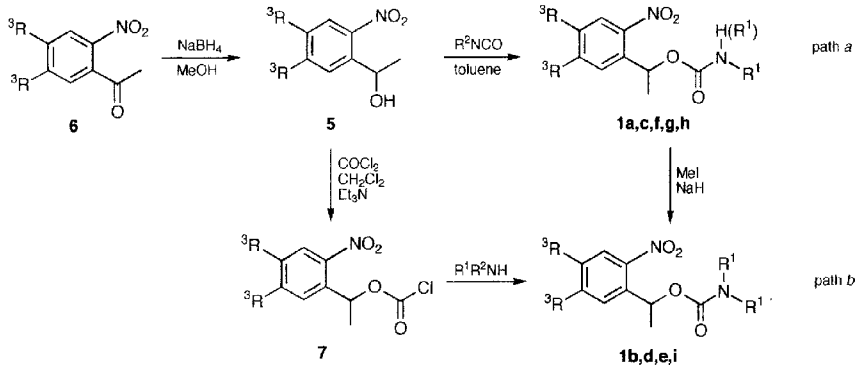
The work described here was aimed at the design and synthesis of organic photoprecursors of amines, which could be applicable to two-stage photoresist systems. The design criteria included a capacity of the system to photochemically generate free amines from precursors, using long-wavelength UV or visible radiation, and the need for good solubility of the precursors in organic media and their easy synthesis, particularly on a large scale. Such photogenerated amines could then be used during image formation to change the dissolution properties of the resist system in developer solutions, to cause color changes so as to differentiate irradiated and nonirradiated areas and, possibly, to catalyse the base-induced formation of nitrenes from arylsulfoxyurethanes.[8–10] For example, bis-substituted monomers have been prepared and reacted with bis-substituted isocyanates to give polymers (Reaction 1). On irradiation, the polymer systems showed good image definition on development. By incorporation of a pH color change indicator, the image and nonimage areas were clearly differentiated by the color change induced through release of amine. These polymer systems are under development for photolithographic reproduction technology.

In peptide or nucleotide synthesis, where amines must be protected in some way until the final steps, photolabile protecting groups have been developed so as to regenerate the amine by irradiating the system with light.[1] It was decided to develop this concept as a means of making amines available on (photon) demand in a resist or lithographic system.[11] Thus, amines would need to be chemically protected by suitable masking groups which, on irradiation, could be cleaved to regenerate the amine. For practical purposes, this photocleavage should be effected by visible or long-wavelength UV light and should have a high quantum efficiency. With the criteria just discussed, the 2-nitrobenzyl functionality[12] was selected as a photolabile protecting group for amines. The 2-nitrobenzyl compounds, in which the benzylic group bears at least one α-hydrogen atom, are known to undergo photoinduced intramolecular oxygen transfer[12] with reduction of the nitro group to nitroso and simultaneous oxidation of the benzylic carbon side-chain. The process is initiated by photoinduced hydrogen abstraction by an ortho nitro group from the nearby benzylic carbon functionality, followed by transfer of a hydroxyl group from nitro back onto the carbon from which the hydrogen was abstracted. This reaction suggested that urethanes of general structural formula (**1**, Scheme 1) should undergo light-induced internal rearrangement to produce a nitroso derivative **2** and a carbamic acid **3**. Because the latter are known to be thermally unstable,[13] their formation should be followed rapidly by spontaneous release of carbon dioxide to give the free amine **4**. Thus, suitably functionalized urethanes should act as photoprecursors of amines and, as such, might be used as photoactive compounds for photoimaging.

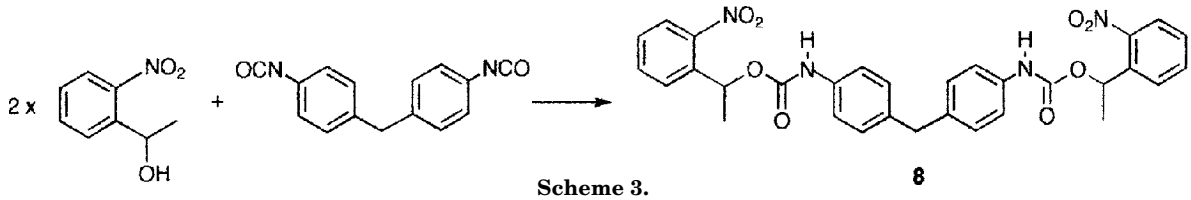
During the course of this work,[11] a patent application[14] on an efficient photodecomposition of arylure-thanes flanked by two ortho nitro groups appeared as a follow up to similar research reported earlier.[15] This last and the present work are complementary in attempting to improve photoefficiency of the reaction. In the present work, greater photoefficiency is attained through the steric interaction of a methyl group in the benzylic side-chain and just one ortho nitro group. This steric hindrance forces a benzylic hydrogen into close proximity to the acceptor nitro group.[16] For the *bis*-ortho nitro approach, a benzylic hydrogen encounters a nitro group at every half rotation.[15] Although these methods of improving photoefficiencies may be regarded as complementary, in practice, the synthesis in the one case of varied benzylic alcohols bearing two flanking ortho nitro groups is not trivial,[17] whereas preparation of singly ortho nitrated benzylic alcohols having an α-methyl group is relatively straightforward. Secondly, the gain in quantum photo-efficiency from placing two nitro groups ortho to a benzylic carbon (Scheme 1) rather than just one changes from about 0.13 to 0.34; the gain in quantum efficiency from the much simpler approach of having an α-methyl on the benzylic carbon is twice that (from 0.13 to 0.64).

Results and Discussion

Synthesis of Photoprecursors of Amines. Several carbamates of general structural Formula **1** were prepared (Scheme 2 and Table I). Their structures were chosen according to the following parameters: the structure and basicity of the amine to be released, the solubilities of precursors and products, the quantum efficiency of the photochemical change and spectral absorption characteristics of the chromophore. Urethanes prepared from 1-(2-nitrophenyl)-1-ethanol (Compounds **1a-f**, Table I) exhibited maximum long-wavelength absorption near 250 nm, with only a small end-absorption running into the visible region, so that light was absorbed only weakly at 300 to 340 nm. The absorption characteristics of these carbamates are very favorable for creating a base by deep-UV photolithography. However, considering that light sources for lithographic printing plates are mostly preferred in the near-UV region, it was decided to synthesize other 2-nitrobenzyl derivatives having substituents in the aromatic ring that



Scheme 2.



Scheme 3.

TABLE I. Maximum Wavelength of Absorption, λ_{max}, for Urethane Photoprecursors 1a–i of Primary and Secondary Amines

1	R^1	R^2	R^3	λ_{max} (nm)
a	H	C_6H_5	H	206, 238, 254
b	CH_3	C_6H_5	H	207, 238, 255
c	H	$CH_3(CH_2)_3$	H	208, 256
d	C_2H_5	C_2H_5	H	208, 258
e	$(CH_3)_2$	$CH(CH_3)_2$ CH	H	226, 242
f	H	$pNO_2C_6H_4$	H	226, 318
g	H	C_6H_5	OCH_3	260, 296, 350
h	H	$CH_3(CH_2)_3$	OCH_3	248, 316, 346
i	CH_3	$CH_3(CH_2)_3$	OCH_3	248, 318, 347

would induce a bathochromic shift of the 250-nm band. Because of the known bathochromic effect of methoxy groups in aromatic ethers,[18] it was decided to prepare 1-(4,5-dimethoxy-2-nitrophenyl)-1-ethoxycarbonyl derivatives of amines (compounds **1g-i**). As shown in Table I, the 250-nm absorption band maximum shifted to 350-nm, with concomitant end-absorption well into the visible region. These carbamates are very favourable for photo-generation of base in near-UV/visible photolithography. The two sets of urethanes listed in Table I provide one set with absorption characteristics suitable for deep-UV work and another more suitable for the visible or near-UV region. The photogenerated amines were either strong bases (alkylamines) or weak bases (arylamines). Scheme 1 shows that the photogenerated amines were either primary (**1**; R^1 = H, R^2 = alkyl or aryl) or secondary (**1**; $R^1 = R^2$ = alkyl or aryl).

Because of steric interactions between a methyl group attached to the benzylic carbon and an ortho nitro group, the hydrogen to be photochemically transferred is forced close to the nitro group.[16] This proximity of the hydrogen and the nitro group makes the photochemical reaction more efficient.[16a] Accordingly, all the urethanes **1a-i** were prepared from secondary alcohols **5**, which themselves were prepared by hydride reduction of the ketones **6** (Scheme 2). The 2-nitro-4,5-dimethoxyacetophenone (**5**; $R^3 = OCH_3$) was prepared by nitration of 3,4-dimethoxyacetophenone.

Photoprecursors of Primary Amines. These urethanes **1a,c,f,h** were prepared by heating readily available isocyanates, R^2NCO, with the corresponding alcohol, **5**, in toluene under an inert atmosphere (Scheme 2, path *a*; R^1 = H, R^2 and R^3 as in Table I). The reaction generally proceeded in good yield. Because a secondary, sterically crowded alcohol was used as substrate, relatively high reaction temperatures were needed and reaction times were heavily dependent on the structure of the isocyanate. The 4-nitrophenylisocyanate was slower to react than phenylisocyanate, which in turn was slower than was butylisocyanate. Crude products were purified by column chromatography and/or recrystallization. The required secondary alcohols **5** were prepared by reduction of the corresponding ketones **6** with sodium tetrahydroborate. Similar methodology was extended to the preparation of the *bis*-urethane **8**, a photoprecursor of 4,4′-diaminodiphenylmethane (Scheme 3).

Photoprecursors of Secondary Amines. Urethanes **1d,e**, photogenerators of secondary amines, required the synthesis of chlorocarbonates (carbonyl chlorides; **7**; Scheme 2, path *b*) from the requisite alcohol and carbonyl chloride, followed by reaction with the desired secondary amine. Urethane photoprecursors **1d,e** of diethylamine and diisopropylamine were obtained in this manner. For successful preparation of the chlorocarbonates **7**, a constant large excess of phosgene was needed to suppress formation of the *bis*-carbonate **9**. Under these conditions, the required chlorocarbonates **7** were obtained in over 90% yield.

The reaction of chlorocarbonates **7** with a secondary amine was dependent on the basicity as well as the degree of steric crowding around the amino nitrogen. The chlorocarbonate reacted easily with *N*,*N*-diethylamine and even with the bulky *N*,*N*-diisopropylamine but reacted only slowly with aniline and did not react at all with *N*-methylaniline. To make this last compound, *N*-[1-(2-nitrophenyl)-1-ethoxycarbonyl]-*N*-methylphenylamine **1b** ($R^1 = CH_3$, R^2 = Ph, R^3 = H), which could be a photoprecursor of *N*-methylaniline, the previously prepared photoprecursor **1a** (R^2 = Ph, $R^1 = R^3$ = H) was methylated[18] with methyl iodide and sodium hydride in DMF. The same methylation strategy was extended to the preparation of *N*-[1-(4,5-dimethoxy-2-nitrophenyl)-1-ethoxycarbonyl]-*N*-methyl-*N*-butylamine **1i** ($R^1 = CH_3$, R^2 = butyl, $R^3 = OCH_3$), a photoprecursor of *N*-methyl-*N*-butylamine, from *N*-[1-(4,5-dimethoxy-2-nitrophenyl)-1-ethoxycarbonyl]-*N*-butylamine **1h** (R^1 = H, R^2 = butyl, $R^3 = OCH_3$).

Photolysis of Carbamates 1a-i. Irradiation was carried out with an Oriel 500-W Hg(Xe) arc lamp. The spectral output of these lamps is a continuum covering the deep-UV to the near IR region, with strong Hg emission lines at 365, 405, and 436 nm; these are the lines of principal interest for UV/visible lithography. Accurate quantum efficiencies were not determined in these preliminary experiments because a typical working lamp was used rather than one from which wavelengths could be selected. Typically, the carbamate to be photolysed was dissolved in an appropriate solvent (tetrahydrofuran, methanol, or benzene) and part of the resulting solution was transferred to either a quartz or a pyrex vessel, depending on the UV/visible absorption characteristics of the carbamate. The solution was deaerated by passing through it a stream of nitrogen and it was then irradiated. A similar solution was prepared as a standard and was not irradiated. Analysis of both nonirradiated and irradiated solutions was carried out by TLC and GC-MS at various time intervals. As an example, photolysis of *N*-[1-(2-nitrophenyl)-1-ethoxycarbonyl]-*N*, *N*-diethylamine **1d** is briefly described. A 0.01-M deaerated solution of this carbamate in dry THF was irradiated for 60 min. On photolysis, this compound was expected to decompose with release N, N-diethylamine and formation of 2-nitrosobenzaldehyde. Preliminary analysis of irradiated and nonirradiated solutions by TLC indicated that the initial carbamate had disappeared. GC/MS analysis of these same nonirradiated and irradiated solutions showed that the carbamate **1d** gradually decreased on irradiation and a new substance appeared and increased in quantity. This new substance was identified as *N*,*N*-diethylamine by GC/MS and by comparison with an authentic sample.

It was observed that photoprecursors of primary aliphatic amines, when photolysed in tetrahydrofuran, did not give the expected free amines but yielded the corresponding pyrrole derivatives, resulting from reaction between the photoreleased amines and the tetrahydrofuran, followed by photo-oxidation. When these same carbamates were irradiated in methanol, the corresponding free amines were observed. All carbamates **1a-i** released the expected free amines when photolysed in appropriate solvents.

The *N*-[1-(4,5-dimethoxy-2-nitrophenyl)-1-ethoxycarbonyl]-*N*-butylamine **1h**, a photo-precursor of butylamine for the visible spectral region, was also irradiated on a filter paper, in the presence of a pH dye indicator (bromothymol blue; pH range 6.0 to 7.6). Both carbamate and indicator were poured onto a filter paper as a solution, and the solvent was allowed to evaporate. The remaining absorbed film was exposed to a light source through a hole of 2.5 cm diam for 2 min. A color change (yellow to blue) was rapidly produced in the exposed area of the film (image). In an experiment more related to commercial thin films used in photolithography, carbamate **1h**, together with polystyrene and bromothymol blue, was dissolved in THF and spin-coated onto an anodized aluminium plate. After allowing the solvent to evaporate from the resulting thin yellow coating, this two-component pseudo-photoresist system was irradiated through a hole, for 2 min. Again, a colour change from yellow to blue was observed in the irradiated area, showing that the system had become basic through release of amine.

Conclusions

A strategic range of organic urethane photoprecursors of primary and secondary, aromatic and aliphatic amines was synthesized and irradiated both in solution and as a solid film. Amines were cleanly generated in all cases, indicating that these 2-nitrobenzylcarbamates **1a-i** are suitable photoprecursors of a range of amines of various basicities and functional types. The 2-nitrobenzyl system can be made to a desired spectral range through substitution into the aromatic ring or through use of polycyclic aromatic systems. The corresponding carbamates provide good base-release agents for either UV and/or visible photolithography.

Experimental

Compounds were identified by three or more of the following techniques: melting point, mass spectrometry, infrared spectroscopy, and ^{1}H nuclear magnetic resonance spectroscopy. For known compounds only selected spectroscopic data and/or melting points are quoted here, sufficient to verify identification. Melting points were recorded on a Reichert melting point apparatus and are uncorrected. Mass spectra were obtained on a VG 7070E mass spectrometer by electron ionization at 70 eV. The GC/MS data were recorded on a Perkin-Elmer GC 8500 with an ion trap separator and detector. Infrared spectra were recorded on a Perkin Elmer 1720X FT-IR spectrometer, liquids as films and solids as KBr disks. Nuclear magnetic resonance (NMR) spectra were recorded on either a Bruker WM 250 MHz FT or a Bruker AC 200 FT spectrometer, using tetramethylsilane as internal standard. Ultraviolet/visible spectra were recorded on a Hewlet Packard diode array FT spectrophotometer. Diethyl ether and tetrahydrofuran were freshly dried by refluxing them over sodium/benzophenone prior to use. Other chemicals were used as purchased.

Preparation of Intermediate Compounds. ***2-Nitro-4,5-dimethoxyacetophenone.*** The 3,4-dimethoxyacetophenone (15 g; 83.2 mmol) was added in small amounts to well stirred, ice-cooled nitric acid (sp. gr. 1.42; 90 mL) over a period of 1 h. The final mixture was stirred for one further hour and then poured onto 400 g of crushed ice. When the ice had melted, the resulting yellow solid was filtered off and air-dried. Yellow crystals from ethanol (9.5 g; 50.7% yield), mp 133 to 134°C [lit. (Ref. 20) 133 to 136°C]. Found: C, 53.5; H, 4.9; N, 6.2. Calculated for $C_{10}H_{11}NO_5$: C, 53.4; H, 4.9; N, 6.2%. ^{1}H-NMR, δ ($CDCl_3$): 2.52 (3H, s), 4.00 (6H, s, 6.80 (1H, s), 7.60 (1H, s); IR, ν_{max}: 1525, 1350, 1194, 1105, and 1074 cm^{-1}; MS: m/z 225 [M$^+$].

***1-(2-Nitrophenyl)ethanol* 5 (R^3 = H).** Sodium borohydride (1.2 g; 32 mmol) was added in small portions over a period of 30 min to a stirred solution of 2-nitroacetophenone (10 g; 60.55 mmol) in dry methanol (100 mL). The resulting mixture was stirred at room temperature for a further 4 h, after which TLC indicated complete absence of starting material. Ice water (50 mL) was added to the reaction mixture and the required organic alcohol was extracted with chloroform (3 × 100 mL) to afford a light yellow oil (10.87 g). Purification by flash chromatography[21] on SiO_2, eluting with CH_2Cl_2, gave 1-(2-nitrophenyl)ethanol as a light yellow oil (10.02 g; 98% yield). Found: C, 57.4; H, 5.4; N, 8.4. Calculated for $C_8H_9NO_3$: C, 57.5; H, 5.4; N, 8.4 %. ^{1}H-NMR, δ ($CDCl_3$): 1.55 (3H, d, J = 5.4 Hz), 2.95 (1H, br. s, -OH), 5.35 (1H, q, J = 5.4 Hz), 7.35-7.90 (4H, m); IR, ν_{max}: 3320 (br., OH), 1525, 1350, 1194, 1105 and 1074 cm^{-1}; MS (CI, NH_3): m/z 185 [M + NH_4^+].

***1-(4,5-Dimethoxy-2-nitrophenyl)ethanol* 5 (R^3 = CH_3).** Sodium borohydride (0.5 g; 13.2 mmol) was added in small portions to a stirred mixture of 2-nitro-4,5-dimethoxyacetophenone (5 g; 22.2 mmol) in dry methanol (50 mL) over a period of 10 min. The mixture was stirred overnight at room temperature and then ice water (50 mL) was added to the reaction mixture; the required alcohol was extracted

with chloroform (3 × 50 mL) to give the product as light yellow crystals (from ethanol; 4.2 g; 84% yield), mp 107 to 108°C. Found: C, 52.9; H, 5.8; N, 6.1. Calculated for $C_{10}H_{13}NO_5$: C, 52.9; H, 5.8; N, 6.2%. ^{1}H-NMR, δ ($CDCl_3$): 1.60 (3H, d, J = 5.7 Hz), 3.98 (3H, s), 4.02 (3H, s) 5.58 (1H, q, J = 5.7 Hz), 7.35 (1H, s), 7.60 (1H, s); IR, ν_{max}: 3320 (br., OH), 1524, 1351, 1195, 1105, and 1074 cm^{-1}; MS (CI, NH_3): m/z 228 [M + H$^+$], 245 [M + NH_4]$^+$.

***1-(2-Nitrophenyl)-1-ethoxycarbonyl chloride* 7 (R^3 = H).** Dry dichloromethane (30 mL) was cooled in an ice bath and phosgene was bubbled into it for 30 min, after which a solution of 1-(2-nitrophenyl)ethanol (2 g; 12 mmol) and triethylamine (1.2 g; 12 mmol) in dichloromethane (10 mL) was added over a period of 10 min. The final mixture was stirred for a further 20 min, after which TLC indicated that no starting material was present. The mixture was purged with nitrogen to remove excess of phosgene and the precipitated triethylammonium chloride was filtered off. The filtrate was evaporated to dryness under vacuum at a bath temperature below 40°C to give a yellow oil, which was purified by flash chromatography on SiO_2, eluting with CH_2Cl_2 to afford the required carbonyl chloride as an oil; this was used immediately for the preparation of the required carbamate (2.53 g; 92% yield). ^{1}H-NMR, δ ($CDCl_3$): 1.90 (3H, d, J = 6.3 Hz, 5.75 (1H, q, J = 6.3 Hz), 7.4 to 8.0 (4H, m).

Preparation of Photoprecursors of Amines for Deep-UV Photolithography. In a typical reaction, 1-(2-nitrophenyl)ethanol (1.8 g; 10.8 mmol) in dry toluene (50 mL) was heated to 80°C under an inert atmosphere, at which stage phenyl isocyanate (1.4 mL; 12 mmol) was added and the mixture was stirred at 80°C for a further 14 h. The solvent was removed by evaporation under vacuum to give a yellow oil (3.1 g), which was purified by flash chromatography on SiO_2 eluting with a mixture of chloroform and toluene (3:1). Recrystallization of the resulting solid from toluene/petroleum ether (bp 60 to 80°C) (2:1) gave colorless needles of *N*-[1-(2-nitrophenyl)-1-ethoxycarbonyl]-*N*-phenylamine **1a** (2.5 g; 81% yield), mp 74 to 75°C. Found: C, 63.0; H, 4.9; N, 9.8. Calculated for $C_{15}H_{14}N_2O_4$: C, 63.0; H, 4.9; N, 9.8%. ^{1}H-NMR, δ ($CDCl_3$): 1.72 (3H, d, J = 5.4 Hz), 6.37 (1H, q, J = 5.4 Hz), 6.65 (1H, br. s., N-H), 7.2 to 8.0 (9H, m); IR, ν_{max}: 3296 (N-H), 1727, 1700, 1527 (N-H), 1502, 1444, 1235, 1222, and 1085 cm^{-1}; MS (FAB, 3-NOBA): m/z 287 [M + H]$^+$. Similarly, photoprecursors **1c, 1f,** and **8** were prepared.

***N-[1-(2-nitrophenyl)-1-ethoxycarbonyl]-N-butylamine* 1c.** From 1-(2-nitrophenyl)ethanol (1.71 g; 10.0 mmol) and butyl isocyanate (1.49 g; 15 mmol), as a light-yellow oil (2.0 g; 75% yield). Found: C, 57.8; H, 6.8; N, 10.9. Calculated for $C^{13}H_{18}N_2O_4$: C, 57.7; H, 6.8; N, 10.8%. ^{1}H-NMR, δ ($CDCl_3$): 0.8–1.0 (3H, m) 1.25–1.52 (4H, m), 1.62 (3H, d, J = 5.4 Hz), 3.0–3.3 (2H, m), 4.72 (1H, br. s., N-H), 6.19 (1H, q, J = 5.4 Hz), 7.4–8.0 (4H, m); IR, ν_{max}: 3296 (N-H), 1727, 1701, 1526, 1501, 1444, 1236, 1221, and 1084 cm^{-1}; MS(EI): m/z: 266 [M$^+$].

***N-[1-(2-Nitrophenyl)-1-ethoxycarbonyl]-N-(4-nitrophenyl)amine* 1f.** From 1-(2-nitrophenyl)ethanol (1.0 g; 5.8 mmol) and 4-nitrophenyl isocyanate (1.0 g; 6.1 mmol) as yellow needles (ethyl acetate/ethanol 4:1, 0.75 g; 39.1% yield), mp 163-164°C. Found: C, 54.4; H, 4.0; N, 12.6. Calculated for $C_{15}H_{13}N_3O_6$: C, 54.4; H, 4.0; N, 12.7%. ^{1}H-NMR, δ ($CDCl_3$): 1.75 (3H, d, J = 5.7 Hz), 6.42 (1H, q, J = 5.7 Hz), 7.18 (1H, br. s, N-H), 7.45 to 8.25 (8H, m); IR, ν_{max}: 3296 (N-H), 1727, 1700, 1527, 1503, 1444, 1235, 1222, and 1085 cm^{-1}; MS (FAB, 3-NOBA): m/z 332 [M + H]$^+$.

***N,N'-bis-[1-(2-Nitrophenyl)-1-ethoxycarbonyl]-4,4'-diaminodiphenylmethane* 8.** From 1-(2-nitro-phenyl) ethanol (1.5 g; 9 mmol) and 4, 4'-diisocyanatophenylmethane (MDI) (1.0 g; 4 mmol) as colourless needles (ethyl acetate, 1.98 g; 85% yield), mp 80-82°C. Found: C, 63.8; H, 4.8; N, 9.6. Calculated for $C_{31}H_{28}N_4O_8$: C, 63.8; H, 4.8; N, 9.6%. ^{1}H-NMR, d ($CDCl_3$): 1.70 (6H, δ, J = 5.4 Hz), 3.88 (2H, s) 6.37 (2H, q, J = 5.4 Hz), 6.60 (2H, br. s, N-H), 7.0 to 8.0 (16H, m); IR, ν_{max}: 3296 (N-H), 1727, 1700, 1527, 1502, 1444, 1235, 1222, and 1085 cm^{-1}; MS(FAB, 3-NOBA): m/z 584 [M$^+$], m/z 585 [M+H$^+$].

***N-[1-(2-Nitrophenyl)-1-ethoxycarbonyl]-N,N-diethylamine* 1d.** Diethylamine (4 mL; 18 mmol) was added to a solution of 1-(2-nitrophenyl)-1-ethoxycarbonyl chloride **7** (R^3 = H; 2.0 g; 8.7 mmol) in dichloromethane (50 mL) under an inert atmosphere and the resulting solution was refluxed for 24 h. After addition of water (50 mL), the organic material was extracted with dichloromethane (3 × 30 mL) to give an oil that was purified by flash chromatography on SiO_2 eluting with CH_2Cl_2 to afford the required carbamate as a light-green oil (0.9 g; 45% yield). Found: C, 58.5; H, 6.8; N, 10.5. Calculated for $C_{13}H_{18}N_2O_4$: C, 58.6; H, 6.8; N, 10.5%; ^{1}H-NMR, δ ($CDCl_3$): 1.0 to 1.3 (6H, m), 1.64 (3H, d, J = 5.7 Hz), 3.20-3.48 (4H, m) 6.22 to 6.32 (1H, q, J = 5.7 Hz), 7.2 to 8.0 (4H, m); IR, ν_{max}: 2976, 2937, 1737 1701, 1504, 1404, 1249, 1209, and 1118 cm^{-1}; MS(EI): m/z 266 [M$^+$].

***N-[1-(2-Nitrophenyl)-1-ethoxycarbonyl]-N,N-diisopropylamine* 1e.** 1-(2-Nitrophenyl)-1-ethoxycarbonyl chloride **7** (R^3 = H; 1.4 g; 6 mmol) was dissolved in diisopropylamine (30 mL) under an inert atmosphere and the solution was refluxed for 48 h. The resulting diisopropylammonium chloride was filtered off and the excess of diisopropylamine was removed by evaporation under vacuum to give an oil that was purified by flash chromatography on SiO_2, eluting with CH_2Cl_2 to afford the required compound as a colourless solid. Recrystallization from toluene-petroleum ether (bp 60-80°C) 2:1 gave colourless crystals (1.0 g; 57% yield), mp 40 to 41°C. Found: C, 60.3; H, 7.3; N, 9.3. Calculated for $C_{15}H_{22}N_2O_4$: C, 60.2; H, 7.3; N, 9.3%. ^{1}H-NMR, δ ($CDCl_3$): 1.25 (12H, d, J = 5.5 Hz), 1.68 (3H, d, J = 5.7 Hz), 3.05 to 3.65 (2H, m), 6.26 (1H, q, J = 5.7 Hz), 7.38 to 8.0 (4H, m); IR, ν_{max}: 2976, 2937, 1737, 1701, 1504 1404, 1249, 1209, and 1118 cm^{-1}; MS(EI): m/z 294 [M$^+$].

***N-[1-(2-Nitrophenyl)-1-ethoxycarbonyl]-N-methyl-N-phenylamine* 1b.** *N*-[1-(2-Nitrophenyl)-1-ethoxycarbonyl]-*N*-phenylamine **1a** (1.0 g; 3.4 mmol) in dry dimethylformamide (10 mL) was added to a slurry of sodium hydride (80% w/w; 0.19 g; 3.5 mmol) in dry dimethylformamide (20 mL) under an inert athmosphere. The mixture was stirred at room temperature for 15 min and then methyl iodide (2.1 mL; 34.9 mmol) was added over a period of 10 min. The reaction mixture was warmed to 50°C and stirred at this temperature for a further 30 min. The precipitate of sodium iodide was filtered off and the solvent was removed by evaporation under vacuum to give a viscous oil that was purified by flash chromatography on SiO_2, eluting with CH_2Cl_2 to afford the required compound as a colourless solid. Recrystallization from toluene gave colourless crystals (0.9 g; 86% yield), mp 62 to 63°C. Found: C, 63.4; H, 5.4; N, 9.3. Calculated for $C_{16}H_{16}N_2O_4$: C, 63.5; H, 5.4; N, 9.3%. ^{1}H-NMR, δ ($CDCl_3$):

1.75 (3H, d, J = 5.7 Hz), 3.40 (3H, s), 6.48 (1H, q, J = 5.7 Hz), 7.35 to 8.10 (9H, m); IR, ν_{max}: 2976, 2937, 1737, 1701, 1504, 1404, 1249, 1209, and 1118 cm^{-1}; MS(EI): m/z 300 $[M^+]$.

Preparation of Photoprecursors of Amines for UV/Visible Photolithography. Phenyl isocyanate (1.4 mL; 12 mmol) in toluene (5 mL) was added to a solution of 1-(4,5-dimethoxy-2-nitrophenyl)ethanol (2 g; 8.8 mmol) in dry toluene (50 mL) over a period of 10 min under an inert atmosphere. The mixture was refluxed for 24 h, after which the solvent was removed by evaporation under vacuum to give a thick yellow oil (2.9 g; 95%); this was purified by flash chromatography on SiO_2, eluting with $CHCl_3$ to give *N*-[1-(4,5-dimethoxy-2-nitrophenyl)-1-ethoxycarboxyl]-*N*-phenylamine **1g** as a light yellow oil (2.4 g; 78.6%). Found: C, 58.8; H, 5.1; N, 8.1. Calculated for $C_{17}H_{18}N_2O_6$: C, 58.9; H, 5.2; N, 8.1%. ^{1}H-NMR, δ ($CDCl_3$): 1.70 (3H, d, J = 5.7 Hz), 3.94 (6H, s), 6.53 (1H, q, J = 5.7 Hz), 6.92 (1H, br. s, NH), 7.00 to 7.40 (6H, m), 7.60 (1H, s); IR, ν_{max}: 3296 (N-H), 1726, 1701, 1527, 1502, 1445, 1235, 1221, and 1085 cm^{-1}; MS(CI; NH_3): m/z 364 $[M + NH_4^+]$.

In a similar way, *N*-[1-(4,5-dimethoxy-2-nitrophenyl)-1-ethoxycarboxyl]-*N*-butylamine **1h** was prepared from 1-(4,5-dimethoxy-2-nitrophenyl)ethanol (1 g; 4.4 mmol) and butyl isocyanate (1 mL; 5.9 mmol). Purification by flash chromatography on SiO_2, eluting with $CHCl_3$ gave a light yellow oil, which slowly solidified. Pale yellow plates (from toluene; 1.2 g; 86.4%), mp 58 to 60°C. Found: C, 55.4; H, 6.9; N, 8.5. Calculated for $C_{15}H_{22}N_2O_6$: C, 55.3; H, 6.8; N, 8.6%; ^{1}H-NMR, δ ($CDCl_3$): 0.86 to 1.00 (3H, m), 1.30 to 1.60 (4H, m), 1.65 (3H, d, J = 6 Hz), 3.10–3.35 (2H, m), 3.98 (3H, s), 4.00 (3H, s), 4.80 (1H, br. s, NH), 6.40 (1H, q, J = 6 Hz), 7.00 (1H, s), 7.60 (1H, s); IR, ν_{max}: 3296 (N-H), 1727, 1701, 1526, 1501, 1444, 1236, 1221, and 1084 cm^{-1}; MS(CI, NH_3): m/z 344 $[M + NH_4]^+$.

Carbamate **1i** was obtained from this last carbamate **1h** by *N*-alkylation: *N*-[1-(4,5-dimethoxy-2-nitrophenyl)-1-ethoxycarboxyl]-*N*-butylamine **1h** (1.0 g; 3.4 mmol) in dry dimethylformamide (10 mL) was added to a slurry of sodium hydride (80% w/w; 0.19 g; 3.5 mmol) in dry dimethylformamide (20 mL) under an inert athmosphere. The mixture was stirred at room temperature for 15 min and then methyl iodide (2.1 mL; 34.9 mmol) was added over a period of 10 min. The reaction mixture was warmed to 50°C and stirred at this temperature for another 30 min. The resulting sodium iodide was filtered off and the solvent was removed by evaporation under vacuum to give a viscous oil. Purification by flash chromatography on SiO_2, eluting with CH_2Cl_2, afforded *N*-[1-(4,5-dimethoxy-2-nitrophenyl)-1-ethoxycarboxyl]-*N*-butyl-*N*-methylamine **1i** as a light yellow oil (0.84 g; 84% yield). Found: C, 56.4; H, 6.5; N, 8.2. Calculated for $C_{16}H_{16}N_2O_4$: C, 56.4; H, 6.5; N, 8.2%. ^{1}H-NMR, δ ($CDCl_3$): 0.86 to 1.00 (3H, m), 1.29 to 1.59 (4H, m), 1.65 (3H, d, J = 6 Hz), 2.95 (3H, s), 3.20 to 3.40 (2H, m), 3.98 (3H, s), 4.00 (3H, s), 4.80 (1H, br. s, NH), 6.40 (1H, q, J = 6 Hz), 7.00 (1H, s), 7.60 (1H, s); IR, ν_{max}: 1737, 1701, 1504, 1404, 1249, 1209 and 1118 cm^{-1}; MS(CI, NH_3): m/z 358 $[M + NH_4]^+$.

Photolysis of the Carbamates in Solution. Typically, *N*-[1-(2-nitrophenyl)-1-ethoxycarbonyl-*N,N*-diethylamine **1d** (0.067 g) was dissolved in dry, distilled THF (25 mL). A portion of this 10^{-2} M solution (10 mL) was transferred to a quartz tube and purged with a stream of nitrogen for 15 min. The deaerated solution was irradiated with the 500-W Hg(Xe) arc lamp for 60 min. Samples of irradiated and nonirradiated solutions were qualitatively analysed by GC/MS. Analysis of the chromatograms indicated photodecomposition of the carbamate and formation of *N,N*-diethylamine, m/z 73 $[M^+]$.

In a similar way, the other carbamates were photolysed: *N*-[1-(2-nitrophenyl)-1-ethoxycarbonyl-*N*-phenylamine **1a** (0.072 g) in THF (25 mL) was irradiated for 60 min. GC/MS analysis of the solutions indicated decomposition of the starting carbamate with formation of aniline, m/z 93 $[M^+]$ and 2-aminoacetophenone, m/z 135 $[M^+]$. *N*-[1-(2-Nitrophenyl)-1-ethoxycarbonyl-*N*-(4-nitrophenyl)amine **1f** (0.083 g) in THF (25 mL) was irradiated for 60 min. GC/MS analysis of the solution indicated decomposition of the starting carbamate with formation of 4-nitroaniline, m/z 138 $[M^+]$ and 2-aminoacetophenone, m/z 135 $[M^+]$. Similarly, *N*-[1-(2-nitrophenyl)-1-ethoxycarbonyl-*N*-butylamine **1c** (0.070 g) in methanol (25 mL) was irradiated for 60 min to form butylamine, m/z 73 $[M^+]$ and 2-aminoacetophenone, m/z 135 $[M^+]$. The *N*-[1-(2-nitrophenyl)-1-ethoxycarbonyl-*N,N*-diisopropylamine **1e** (0.075 g) in THF (25 mL) irradiated for 60 min gave *N,N*-diisopropylamine, m/z 102 $[M + H]^+$ and 2-aminoacetophe-none, m/z 135 $[M^+]$. The *N*-[1-(2-Nitrophenyl)-1-ethoxycarbonyl-*N*-methyl-*N*-phenylamine **1b** (0.076 g) in THF (25 mL) irradiated for 60 min gave *N*-methyl-*N*-phenylamine, m/z 107 $[M^+]$ and 2-aminoacetophenone, m/z 135 $[M^+]$. The *N*-[1-(4,5-dimethoxy-2-nitrophenyl)-1-ethoxycarbonyl-*N*-butylamine **1h** (0.080 g) in methanol (25 mL) irradiated for 60 min afforded butylamine, m/z 73 $[M^+]$ and 4,5-dimethoxy-2-nitrosoacetophenone, m/z 177 $[M^+]$. The *N*-[1-(4'-5'-dimethoxy-2-nitrophenyl)-1-ethoxycarbonyl-*N*-phenylamine **1g** (0.072 g) in THF (25 mL) irradiated for 60 min gave aniline, m/z 93 $[M^+]$ and 4,5-dimethoxy-2-nitrosoacetophenone, m/z 177 $[M^+]$. The *N'*-bis-[1-(2-nitrophenyl)-1-ethoxycarbonyl]-4,4'-diaminodiphenylmethane **8** (0.15 g) in THF (25 mL) gave *bis*(4-aminophenyl)methane, m/z 199 $[M + H]^+$, 2-nitrosoacetophenone, m/z 150 $[M + H]^+$, 2-aminoacetophenone, m/z 135 $[M^+]$ and 2-nitroace-tophenone, m/z 166 $[M + H]^+$.

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References

1. A. Patchornick, B. Amit and R. B. Woodward, *J. Amer. Chem. Soc.* **92,** 6333 (1970); V.N.R. Pillai, *Synthesis,* 1 (1980).
2. E. Reichmanis, S. A. MacDonald and T. Iwayanagi in *Polymers for Microlithography: Materials and Processes*, F.M. Houlihan, Ed., ACS Symposium Series 412, Washington, DC, 1989, Chap. 1.
3. R. Srinivasan, *J. Vac. Sci. Technol. B* **1**, 923 (1983); P. Dufour in *Chemistry and Technology of UV and EB Formulation for Coatings, Inks and Paints,* Vol. **1**, P. K. T. Goldring, Ed., SITA Technology, London, 1991, pp. 15–30; C. Kutal, S. K. Weit and C. G. Willson, *Polym. Mater. Sci. Eng.* **61**, 195 (1989); J. Speight in *The Chemistry of the Semiconductor Industry,* S. J. Moss and A. Ledwith, Eds., Blackie, Glasgow, 1987, pp. 1–16.
4. J. F. Rabek, *Mechanisms of Photochemical Processes and Photochemical Reactions in Polymers,* Wiley, Chichester, 1987, p. 462.
5. B. M. Monroe, *Radiation Curing: Science and Technology,* S. P. Pappas, Ed., Plenum Press, New York, 1992, p. 399.
6. J. F. Cameron and J. M. J. Fréchet, *J. Org. Chem.* **55,** 5919 (1990); J. F. Cameron, C. G. Willson, and J. F. J. Fréchet, *J. Chem. Soc. Chem. Commun.*, 923 (1995).
7. J. E. Trend and G.L. Eian, *Colloids and Surfaces in Reprographic Technology,* ACS Symposium Series 200, Washington, DC, 1982, pp. 371–381; *Chem. Abstr.* **97,** 227300p (1982).
8. W. Lwowski, T. J. Maricich and T. W. Mattingley, *J. Am. Chem. Soc.* **85**, 1200 (1963).
9. F. Bosold and G. Boche, *Angew. Chem. Int. Edn. Engl.,* **29,** 63 (1990).
10. M. Novak, K. A. Martin, J. L. Heinrich, K. M. Peet, and L. K. Mohler, *J. Org. Chem.*, **55,** 3023 (1990).
11. M. L. S. Cristiano, PhD Thesis, Faculty of Science, University of Liverpool, 1993, p.211.
12. P. De Mayo and S. T. Reid, *Quart. Rev.* (London) **15,** 414 (1961).
13. D. P. N. Satchell and R. S. Satchell, *Chem. Soc. Rev.* **4,** 231 (1975); J. March, *Advanced Organic Chemistry,*Wiley, New York, 1992, p. 886.

14. C. F. Kahle, N. D. McMurdie, R. O. Kollah, D. E. Rardon, and G. J. McCollum, *PCT*/US95/08121, 13th July, 1994.
15. J. F. Cameron and J. M. J. Frechet, *J. Am. Chem. Soc.* **113,** 4303–4307 (1991).
16. (a) E. Reichmanis, B. C. Smith and R. Gooden, *J. Polymer Sci., Polymer Chem. Edn.* **23,** 1 (1985); (b) J. A. Barltrop, P. J. Plant and P. Schofield, *J. Chem. Soc. Chem. Commun.,* 822 (1996); and see Ref. 1.
17. C. F. Kahle, R. O. Kollah and G. J. McCollum, *U.S. Patent* 5,449,834, 12th Sept., 1995, *Chem. Abstr.* **124,** 86588*m* (1996).
18. See, for example, A. J. Gordon and R. A. Ford, *The Chemist's Companion,* Wiley, New York, 1972, p. 215 and references cited therein or H. H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy,* Wiley, New York, 1962, 257–266.
19. G. Marino, L. Valente, R. A. W. Johnstone, F. Mohammedi-Tabrizi, and G. C. Sodini, *J. Chem. Soc., Chem. Commun.,* 357 (1972).
20. J. L. Minielli and H. C. Scarborough, *Fr. Pat.* **M**3207 (1965); *Chem. Abstr.* **63,** 13287a (1967).
21. W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.* **43,** 2923 (1978).