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Design and Synthesis of a Photoaromatization-Based Two-Stage Photobase Generator for Pitch Division Lithography

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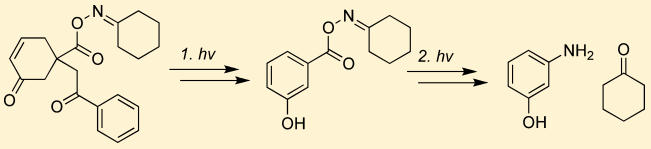
Supporting Information

ABSTRACT: The synthesis of a two-stage photobase generator (PBG) based on photoinduced aromatization is described. This material was designed for use in resolution-enhanced photolithography. Computer modeling predicts that a delay in the onset of base generation can lead to improved image quality. This delay can be realized by a PBG that must undergo two sequential photoreactions for each molecule of base generated. Toward that end, latent PBGs were designed that are oxime esters of aliphatic acids, which undergo Norrish type II reactions to yield oxime esters of aromatic acids that are efficient PBGs.



INTRODUCTION

The microelectronics manufacturing industry is taking extreme measures to extend the resolution limit of current 193 nm tools beyond their physical limits in order to keep pace with Moore's Law.[1] These extreme measures come at the cost of several added processing steps, which lead to increased production costs.[2] We have previously demonstrated a "trick" that exploits chemistry to double the resolution of 193 nm lithography and does not require any extra processing steps. The trick only requires adding a photobase generator (PBG) to the formulation of a typical 193 nm resist.[3] If the stoichiometry and the kinetics are right, the image recorded in such a resist has twice the pitch of the projected mask image. Unfortunately, when sub-100 nm features are printed, they suffer from line edge roughness (LER). This LER is undoubtedly caused by the convolution of several issues, but we believe that the major contributor is the fact that the slope of the acid concentration gradient at the line edge is not as steep as it is in normal imaging.

Modeling suggests that a delay in onset of base generation as a function of dose would increase the fidelity of the printed image.[4] Therefore a "two-stage" PBG was designed, one that requires a sequence of two photolysis reactions to generate a molecule of base. If a latent PBG reacts with a photon to produce an active PBG that can in turn react with a second photon to produce base, and the relative rates of the reactions are closely matched, a significant delay in base generation can be realized, which results in steepening the gradient of the net acid generation curve. This paper describes the design and synthesis of a two-stage PBG based on photoinduced aromatization.

RESULTS AND DISCUSSION

Oxime esters of aromatic acids are a well-studied class of PBGs.[5] Oxime esters of aliphatic acids do not produce base at a significant rate upon exposure at 193 nm, but aromatic analogues are efficient PBGs. Therefore, an oxime ester of an aliphatic acid that undergoes photoaromatization reaction to create an active, aromatic PBG can serve as the latent PBG, as depicted in Scheme 1.

First Approach. Several examples of photoaromatization reactions are known, but most are based on 1,4-dihydropyridines[6] or more complicated systems that are not suited for our purpose.[7,8] A basic design for a photoaromatization type two-stage PBG is illustrated in Scheme 1, based on a photoaromatization mechanism achieved by the Norrish type II photoelimination.[9] A major obstacle in this design is the fact that dienes are efficient triplet quenchers. Luckily, they are not efficient singlet quenchers. Wagner teaches that the strength of the γ-CH bond of the ketone dictates whether the type II reaction proceeds via the singlet or triplet state.[10] Clearly, we needed a singlet pathway. According to Wagner's studies, ketones with stronger γ-CH bonds, such as those in 2-pentanone (98 kcal/mol), proceed via a triplet state, whereas those with weaker γ-CH bonds, such as 5-methyl-2-hexanone (91 kcal/mol), proceed mostly via the singlet.[9] As shown in Scheme 2, compound **5a** is an oxime ester of cyclohexyldienylcarboxylic acid with an allylic and tertiary γ-hydrogen. On the basis of Wagner's studies, we hoped that

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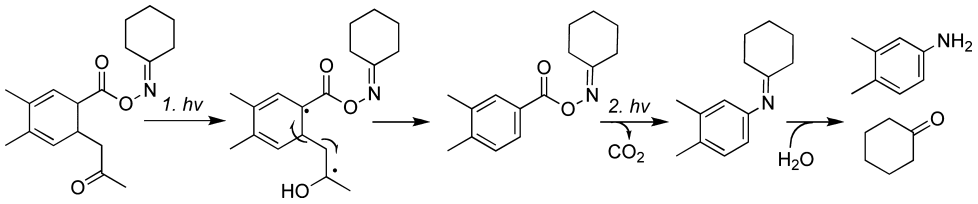
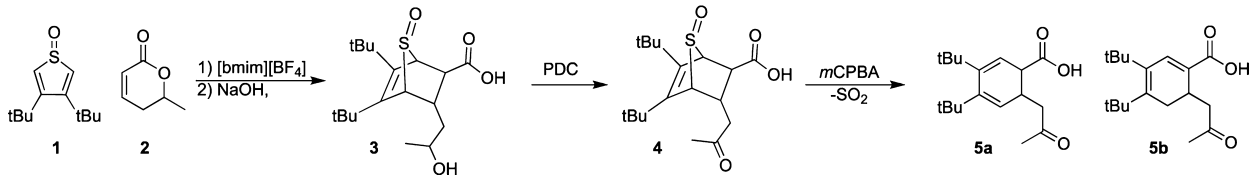
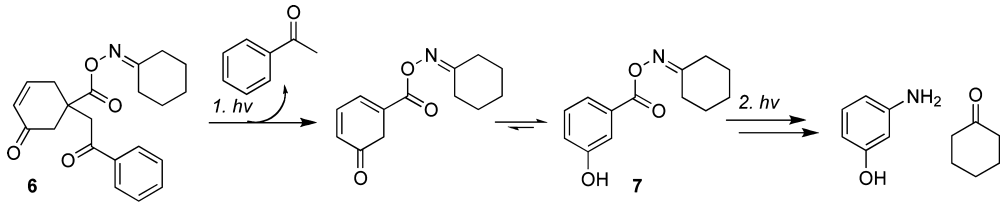
Scheme 1. First Design Approach of a Two-Step PBG



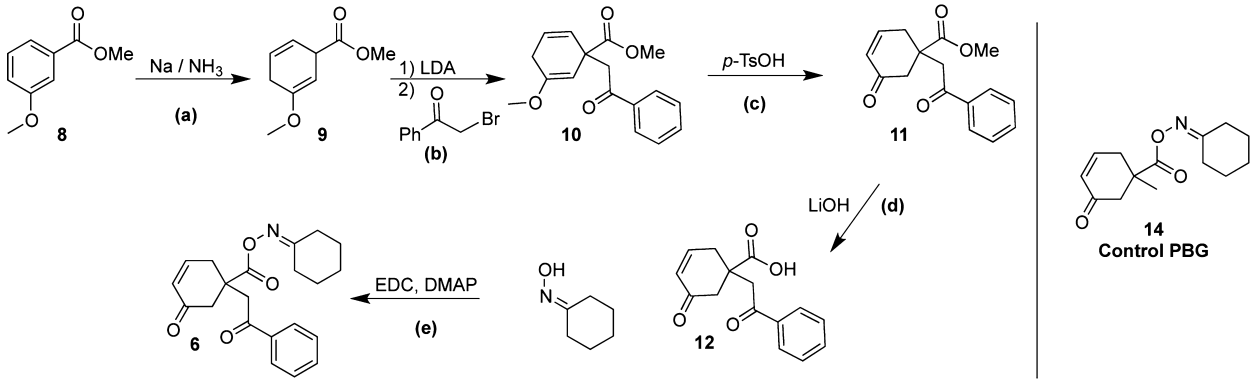
Scheme 2. Synthesis of 5a,b



Scheme 3. Second Design Approach of a Two-Step PBG



Scheme 4. Synthesis of 13



this compound would undergo a fast type II cleavage and aromatization via the singlet manifold.

We envisioned making the cyclohexadiene platform via a Diels–Alder (D–A) reaction (Scheme 2). The dienophile is well-suited for installation of the oxime ester due to its electron-withdrawing properties and offers a means to incorporate various photolabile moieties as substituents on the alkene. We predicted that the D–A adduct of thiophene dioxide and our tailored dienophile could lead to the cyclohexadiene through loss of SO_2. Unfortunately, thiophene dioxide dimerizes at a lower temperature than that required to activate the addition of the desired dienophile (Supporting Information Figure S4). Only traces of the cross-products could be detected. Previous work by Nakayama[11] demonstrated that sufficiently bulky substituents, such as *t*-butyl in the 3,4 position of the thiophene, block the dimerization and allow for cross D–A reactions. The use of parasorbic acid as the dienophile was appealing since it set the position of the ester alpha to the cyclohexyl backbone and could be hydrolyzed to give a methyl ester and a secondary alcohol which can be oxidized to the desired ketone. The first attempts at the D–A reaction were not successful, presumably because the dioxide is too strongly electron-withdrawing, but luckily, the reaction proceeded smoothly with thiophene oxide. Attempts were made to oxidize the secondary alcohol and the sulfoxide simultaneously to facilitate SO_2 loss, but these reactions gave mixtures, so a stepwise approach was taken that ultimately provided the desired bicyclic sulfone (**4**).

The expulsion of SO_2 from the sulfone was more facile than expected and proceeded cleanly during silica column chromatography to yield a mixture of cyclohexadiene isomers (**5a,b**). Sadly, exposure of compounds **5a,b** to UV radiation showed no significant photoreactivity under our photolysis conditions. These substances are essentially inert at 248 and 193 nm. Upon prolonged exposure, a complex mixture of products was produced. This disappointing observation could be the result of the fact that the aliphatic ketones in compounds **5a,b** are inefficient light absorbers, whereas the diene chromophore absorbs UV light much more efficiently. Additionally, the intersystem crossing of the singlet to the

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triplet could be faster than abstraction of the γ-hydrogen, in which case energy transfer to the diene would quench the triplet very quickly. Since no photoaromatization was observed for **5a,b**, a new strategy outlined in Scheme 3 was pursued.

Second Approach. The goal of the second design was to avoid a diene in favor of an enone in the first step and to achieve aromatization after elimination via a favorable tautomerization (Scheme 3). Our hope was that while it is well-known that enones also quench triplet states, this structural variation would change the rates in our favor. An additional goal of the second design was to increase the UV absorption efficiency of the chromophore in the first reaction step. Whereas the first design approach depends on absorbance by a weak acetone chromophore, the second design incorporates an acetophenone chromophore, which has 3 orders of magnitude higher molar absorptivity than acetone. The design outlined in Scheme 3 was validated by preliminary exposure studies that showed that the oxime esters of hydroxybenzoic acid perform just as efficiently as their benzoyl oxime counterparts in pitch division formulations.

The synthesis of this new target (**13**) was achieved via a Birch reduction of methyl 3-methoxybenzoate (a) followed by installation of the photolabile groups via enolate chemistry (b) (Scheme 4). Reduction and installation of acetophenone proceeded in acceptable yields, but attempts to cleave the methyl ether and hydrolyze the ester simultaneously were unsuccessful, so these deprotection steps were carried out in sequence (c–d) followed by installation of the oxime via carbodiimide-mediated esterification (e). Even in the absence of extensive reaction optimization, this pathway gave a > 15% yield over six steps and is sufficiently flexible to allow installation of acetophenone derivatives. The two-stage PBG **13** functions effectively in pitch division formulations (Supporting Information Figure S3), but the control PBG **15** does not. On the basis of these functional tests, the details of the photochemistry of these compounds were studied. The results of that work are described in the accompanying paper.[20]

■ CONCLUSION

We have reported a new approach to photoaromatization and a two-stage photoreaction that leads to basic photoproducts. The synthesis of PBG **13** is flexible and allows for modification of the acetophenone moiety.

■ EXPERIMENTAL SECTION

General Information. ^{1}H NMR spectra were recorded on 300 or 400 MHz spectrometers at ambient temperature unless otherwise noted and are reported in parts per million using solvent as the internal standard ($CDCl_3$ at 7.26 ppm or CD_3OD at 3.31 ppm). Data are reported as multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant(s) in hertz. ^{13}C NMR spectra were recorded on a 75 or 100 MHz spectrometer. Chemical shifts are reported in parts per million from tetramethylsilane, with the residual solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm). High-resolution mass spectra (HRMS) by ESI-QTOF are reported as *m*/*z* (relative intensity). UV light exposures were performed at 248 nm using a KrF excimer laser, and the 193 nm exposures were carried out with a ArF excimer laser. Films were spin-coated on a Brewer CEE 100CB spin coater. Film thicknesses were determined with an ellipsometer using wavelengths from 382 to 984 nm with a 65° angle of incidence. A hot plate open to air was used to bake the photoresists.

3,4-Di-*tert*-butylthiophene-1-oxide was synthesized according to the work of Nakayama, and the spectroscopic properties matched those reported in literature.[11,12]

4-Hydroxy-6-methyltetrahydro-2*H*-pyran-2-one was synthesized according to the procedure of Dumesic and Chia[13] on a 119 mmol scale to provide 15.2 g (117 mmol, 98%) of product.

6-Methyl-5,6-dihydro-2*H*-pyran-2-one (2) was synthesized according to the procedure of Sato and co-workers[14] on a 117 mmol scale to provide 4.57 g (40.8 mmol, 35%) of product with spectroscopic properties that match those reported in literature.[15]

7-Thiabicyclo[2.2.1]hept-5-ene-2-carboxylic Acid, 3-(Propan-2-ol)-oxide (3). A solution of 3,4-di-*tert*-butylthiophene-1-oxide (0.177 g, 0.832 mmol, 1 equiv) and parasorbic acid (**2**) (0.121 g, 1.00 mmol, 1.2 equiv) in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4, 1.0 g) was heated to 120 °C and stirred for 16 h. The reaction was partitioned between Et_2O and H_2O, and the organic layer was dried ($MgSO_4$) and then concentrated in vacuo. The crude colorless oil (0.270 g) was dissolved in MeOH and chilled to 0 °C before treating with NaOH (2 M in H_2O) then warmed to rt while stirring for 16 h. The reaction was quenched with HCl (1 N in H_2O) until the reaction solution was at pH 1 and then extracted with EtOAc (150 mL). The organic layer was washed with H_2O (2 × 50 mL) and brine (1 × 50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The colorless oil was then purified by trituration in acetone and hexane at 0 °C to yield 0.260 g (0.760 mmol, 91%) of a white powder, mp 151–154 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 4.61–4.53 (m, 1H), 4.27–4.16 (m, 1H), 3.99–3.87 (m, 1H), 3.50–3.47 (m, 1H), 3.19–3.08 (m, 2H), 2.09 (s, 3H), 1.22–1.15 (m, 18H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 171.9, 143.7, 141.5, 74.5, 69.5, 67.3, 34.6, 33.5, 31.9, 31.8, 30.6, 29.4, 20.0. IR (neat): 3216, 2965, 1712, 1204, 1000. HRMS: exact mass calcd for $C_{18}H_{30}O_4S$ $[M + Na]^+$ 365.1762, found 365.1757.

7-Thiabicyclo[2.2.1]hept-5-ene-2-carboxylic Acid, 3-(Propan-2-one)-oxide (4). To a chilled (0 °C) solution of pyridinium dichromate (0.384 g, 1.02 mmol, 3.5 equiv) in DMF (3 mL) was added a solution of compound **3** (0.100 g, 0.292 mmol, 1 equiv) in DMF (3 mL) and warmed to rt while stirring for 16 h. The reaction was partitioned with EtOAc (75 mL) and H_2O (100 mL), and the organic layer was washed with H_2O (50 mL) and brine (50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The reaction yielded 65 mg (0.191 mmol, 65%) of colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ4.18 (s, 1H), 3.95 (s, 1H), 3.42–3.39 (m, 1H), 3.19–2.98 (m, 2H), 2.71–2.61 (m, 1H), 2.05 (s, 3H), 1.16–1.15 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.1, 176.8, 142.4, 69.8, 68.9, 43.5, 41.5, 34.7, 34.4, 33.5, 32.9, 32.5, 32.5, 32.4, 30.1. IR (neat): 2961, 1718. HRMS: exact mass calcd for $C_{18}H_{28}O_4S$ $[M + H]^+$ 340.1708, found 341.1788.

Compounds 5a and 5b. A solution of compound **4** (0.055 g, 0.161 mmol, 1 equiv) and *m*-CPBA (0.033 g, 0.193, 1.2 equiv) in DCM (5 mL) and THF (5 mL) was stirred overnight at rt. The reaction was partitioned between EtOAc (40 mL) and H_2O (50 mL), and the organic layer was washed with H_2O (50 mL) and brine (50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude yellow oil was purified by flash chromatography (silica gel 2:1 = Hex/EtOAc) to yield a mixture of isomers of compound **5** as a colorless oil (0.030 g, 0.102 mmol, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.51 (d, *J* = 7.2 Hz, 1H), 5.95 (s, 1H), 4.89 (s, 1H), 3.89 (s, 1H), 3.25 (m, 2H), 3.0 (m, 1H), 2.78–2.45 (m, 6H), 2.19–2.16 (m, 6H), 1.78–1.64 (m, 1H), 1.55–1.51 (m, 4H), 1.29–1.66 (m, 34H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.3, 206.2, 174.2, 172.9, 153.6, 150.2, 131.7, 127.9, 96.4, 92.8, 76.2, 71.6, 47.6, 45.6, 44.1, 43.1, 37.7, 37.5, 37.32, 36.33, 32.9, 30.7, 30.0, 29.0. IR (neat): 1749, 1721. HRMS: exact mass calcd for $C_{18}H_{28}O_3$ $[M + Na]^+$ 315.1936, found 315.1931.

Cyclohexanone *O*-(3-Hydroxybenzoyl)oxime (7). To a chilled solution (0 °C) of 3-hydroxybenzoic acid (3.0 g, 21.7 mmol, 1 equiv), cyclohexanone oxime (2.5 g, 21.7 mmol, 1 equiv), and *N*,*N*-dimethyl-4-aminopyridine (0.27 g, 2.2 mmol, 0.1 equiv) in dichloromethane (150 mL) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (4.16 g, 21.7 mmol, 1 equiv) and stirred for 1 h at 0 °C. Upon warming to rt and stirring for an additional 4 h, the reaction mixture was quenched with saturated $NaHCO_3$ (2 × 100 mL), water

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(1 × 100 mL), and brine (1 × 100 mL). The organic layer was subsequently dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting crude pale yellow solid was purified by flash chromatography (silica gel 4:1 = Hex/EtOAc) to yield cyclohexanone *O*-(3-hydroxybenzoyl)oxime as a white solid (1.5 g, 6.4 mmol, 30% yield), mp 134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63−7.53 (m, 2H), 7.27 (t, J = 8.1 Hz, 1H), 7.17−7.12 (m, 1H), 2.60 (t, J = 6.0 Hz, 2H), 2.35 (t, J = 6.0 Hz, 2H), 1.74−1.52 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 165.1, 156.7, 130.1, 129.7, 121.3, 121.1, 116.6, 23.0, 27.2, 26.8, 25.9, 25.4. IR (neat): 1720, 2930, 2861, 3356. HRMS: exact mass calcd for $C_{13}H_{15}NO_3$ $[M + Na]^+$ 256.0950, found 256.0946.

Methyl 3-Methoxycyclohexa-2,5-dienecarboxylate (9). The following procedure was adapted from the method of Rabideau.[16−18] A solution of methyl 3-methoxybenzoate (5.00 g, 30.1 mmol, 1 equiv) in THF (50 mL) was cooled to −78 °C, and then H_2O (0.81 g, 45.1 mmol, 1.5 equiv), NH_3 (100 mL), and sodium (1.0 g, 45.1 mmol, 1.5 equiv) were added, and the resulting mixture was stirred for 30 min at −78 °C. The mixture was quenched with a concentrated NH_4Cl solution and then stirred for 30 min at rt, extracted with ethyl acetate (3 × 100 mL), and the combined organic layers were washed with water (2 × 150 mL) and brine (1 × 100 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting oil was purified by flash chromatography (silica gel 20:1 = Hex/EtOAc) to yield 3-methoxycyclohexa-2,5-dienecarboxylate as a colorless oil (2.80 g, 16.6 mmol, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.80−5.68 (m, 2H), 4.72−4.62 (m, 1H), 3.87−3.74 (m, 1H), 3.61 (s, 3H), 3.51 (s, 3H), 2.69−2.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.5, 154.4, 125.1, 122.2, 89.5, 53.8, 51.9, 42.9, 28.3. IR (neat): 1724, 1194, 1166. HRMS: exact mass calcd for $C_9H_{12}O_3$ $[M + H]^+$ 169.0865, found 169.0859.

Methyl 3-Methoxy-1-(2-oxo-2-phenylethyl)cyclohexa-2,5-dienecarboxylate (10). To a chilled (−10 °C) solution of diisopropylamine (1.80 g, 18.8 mmol, 1.2 equiv) in THF (30 mL) was added 2.5 M solution of *n*-BuLi in hexanes (7.50 mL, 18.8 mmol, 1.2 equiv) and stirred for 30 min. The reaction mixture was cooled to −78 °C, and methyl 3-methoxycyclohexa-2,5-dienecarboxylate (2.60 g, 15.5 mmol 1 equiv) was added dropwise. After stirring for 15 min, 2-bromoacetophenone (6.20 g, 31.0 mmol, 2 equiv) in hexamethylphosphoric triamide (15 mL) was added, and the reaction mixture was stirred for 30 min at −78 °C. Upon warming to rt and stirring for an additional 2 h, the reaction mixture was partitioned with H_2O and EtOAc. The organic layer was washed with H_2O (2 × 150 mL) and brine (1 × 100 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting crude oil was purified by flash chromatography (silica gel 10:1 = Hex/EtOAc) to yield methyl 3-methoxy-1-(2-oxo-2-phenylethyl)cyclohexa-2,5-dienecarboxylate as a pale yellow oil (4.1 g, 14.2 mmol, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93−7.83 (m, 2H), 7.55−7.46 (m, 1H), 7.45−7.35 (m, 2H), 5.92−5.83 (m, 1H), 5.79 (dt, J = 9.9 and 3.3 Hz, 1H), 4.83−4.78 (m, 1H), 3.68 (s, 3H), 3.51 (s, 3H), 3.44 (s, 2H), 2.80−2.59 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.2, 175.2, 154.6, 136.6, 133.2, 128.5, 128.0, 127.1, 124.6, 95.0, 54.0, 52.4, 50.1, 47.4, 28.6. IR (neat): 1723, 1683. HRMS: exact mass calcd for $C_{17}H_{18}O_4$ $[M + H]^+$ 287.1283, found 287.1273.

Methyl 5-Oxo-1-(2-oxo-2-phenylethyl)cyclohex-3-enecarboxylate (11). To a solution of methyl 3-methoxy-1-(2-oxo-2-phenylethyl)cyclohexa-2,5-dienecarboxylate (2.0 g, 7.0 mmol, 1 equiv) in 1,4-dioxane (50 mL) and H_2O (10 mL) was added *p*-toluenesulfonic acid monohydrate (1.3 g, 7.0 mmol, 1 equiv), and the mixture was then heated to 100 °C and stirred for 1.5 h and cooled to rt. The reaction mixture was then extracted with EtOAc (200 mL), and the organic layer was washed with saturated $NaHCO_3$ (1 × 100 mL), H_2O (1 × 100 mL), and brine (1 × 100 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude oil was then purified by flash chromatography (silica gel 4:1 = Hex/EtOAc) to yield methyl 5-oxo-1-(2-oxo-2-phenylethyl)cyclohex-3-enecarboxylate as a white solid (0.98 g, 3.6 mmol, 52%), mp 112−114 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92−7.85 (m, 2H), 7.62−7.55 (m, 1H), 7.45 (t, J = 7.8 Hz, 2H), 6.87 (dt, J = 9.9 and 4.2 Hz, 1H), 6.08 (dt, J = 9.9 and 1.8 Hz, 1H), 3.67 (s, 3H), 3.52−3.36 (m, 2H), 3.06−2.97 (m, 1H), 2.98 (d, J = 16.2 Hz, 1H), 2.68−2.59 (m, 1H), 2.56 (d, J = 16.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.7, 196.5, 175.1, 146.8, 136.5, 133.7, 129.5, 128.8, 128.1, 52.7, 46.0, 45.5, 45.0, 33.7. IR (neat): 1726, 1673. HRMS: exact mass calcd for $C_{16}H_{16}O_4$ $[M + H]^+$ 273.1127, found 273.1126.

5-Oxo-1-(2-oxo-2-phenylethyl)cyclohex-3-ene carboxylic acid (12). To a chilled solution (0 °C) solution of methyl 5-oxo-1-(2-oxo-2-phenylethyl)cyclohex-3-enecarboxylate (1.20 g, 4.41 mmol, 1 equiv) in THF (60 mL) was added a solution of lithium hydroxide (116 mg, 4.85 mmol, 1.1 equiv) in H_2O (60 mL), and the resulting solution was stirred for 1 h, warmed to rt, and stirred for an additional 2 h then quenched with 1 N HCl (10 mL) and partitioned between EtOAc (100 mL) and H_2O (50 mL). The organic layer was washed with brine (1 × 50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting yellow solid was purified by flash chromatography (silica gel 2:1 = Hex/EtOAc) to yield 5-oxo-1-(2-oxo-2-phenylethyl)-cyclohex-3-enecarboxylic acid as a pale yellow solid (1.0 g, 3.9 mmol, 90% yield), mp 149−151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06−7.85 (m, 2H), 7.72−7.58 (m, 1H), 7.58−7.42 (m, 2H), 7.00−6.82 (m, 1H), 6.05−5.93 (m, 1H), 3.56 (d, J = 18.3 Hz, 1H), 3.45 (d, J = 18.3 Hz, 1H), 2.90 (d, J = 16.5 Hz, 1H), 2.90−2.76 (m, 1H), 2.72−2.58 (m, 1H), 2.45 (d, J = 16.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.5, 197.4, 176.5, 147.5, 137.6, 134.4, 129.8, 129.7, 128.9, 46.8, 46.3, 45.6, 35.0. IR (neat): 2909, 1697, 1678. HRMS: exact mass calcd for $C_{15}H_{14}O_4$ $[M + H]^+$ 259.0965, found 259.0962.

5-(((Cyclohexylideneamino)oxy)carbonyl)-5-(2-oxo-2-phenylethyl)cyclohex-2-enone (6). To a chilled solution (0 °C) of 5-oxo-1-(2-oxo-2-phenylethyl)cyclohex-3-enecarboxylic acid (0.18 g, 0.70 mmol, 1 equiv), cyclohexanone oxime (0.11 g, 0.98 mmol, 1.4 equiv), and *N*,*N*-dimethyl-4-aminopyridine (8.6 mg, 0.07 mmol, 0.1 equiv) in DCM (10 mL) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (0.155 g, 0.81 mmol, 1.2 equiv) and stirred for 1 h. Upon warming to rt and stirring for an additional 2 h, the reaction mixture was quenched with saturated $NaHCO_3$ (2 × 50 mL), water (1 × 50 mL), and brine (1 × 50 mL). The organic layer was subsequently dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting crude yellow oil was purified by flash chromatography (silica gel 4:1 = Hex/EtOAc) to yield 5-(((cyclohexylideneamino)-oxy)carbonyl)-5-(2-oxo-2-phenylethyl)cyclohex-2-enone as a pale yellow oil (0.16 g, 0.45 mmol, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90−7.80 (m, 2H), 7.54−7.46 (m, 1H), 7.38 (t, J = 7.8 Hz, 2H), 6.84 (dt, J = 9.9 and 4.2 Hz, 1H), 6.04 (dt, J = 9.9 and 1.8 Hz, 1H), 3.55 (d, J = 18.0 Hz, 1H), 3.40 (d, J = 18.0 Hz, 1H), 3.09 (d, J = 16.5 Hz, 1H), 3.02−2.90 (m, 1H), 2.73−2.61 (m, 1H), 2.56 (d, J = 16.5 Hz, 1H), 2.34 (t, J = 6.3 Hz, 1H), 2.29 (t, J = 6.3 Hz, 1H), 1.71−1.42 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.3, 172.2, 170.2, 146.8, 136.2, 133.5, 129.5, 128.6, 127.9, 46.0, 45.6, 44.8, 34.2, 31.9, 27.1, 26.6, 25.6, 25.2. IR (neat): 2938, 2861, 1747, 1677. HRMS: exact mass calcd for $C_{21}H_{23}NO_4$ $[M + Na]^+$ 376.1525, found 376.1523.

1-Methyl-5-oxocyclohex-3-enecarboxylic Acid (13). The following procedure was adapted from Smith and Richmond.[19] To a chilled solution (−78 °C) of 3-methoxybenzoic acid (1.5 g, 9.9 mmol, 1 equiv) in THF (10 mL) were added ammonia (50 mL) and lithium metal (0.274 g, 39.4 mmol, 4 equiv). The resulting solution was stirred for 1 h at −78 °C, after which a solution of methyl iodide (2.8 g, 19.7 mmol) in THF (2 mL) was then added, and the resulting mixture was stirred for 1 h at −78 °C, quenched with solid ammonium chloride, and the ammonia was then evaporated under a stream of nitrogen. The resulting crude solid was dissolved in HCl (2 N H_2O) and refluxed for 30 min. After cooling, the solution was extracted with EtOAc (600 mL), and the organic fraction was washed with H_2O (2 × 100 mL) and brine (1 × 50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting pale yellow solid was purified by flash chromatography (silica gel 2:1 = Hex/EtOAc) to yield 1-methyl-5-oxocyclohex-3-ene carboxylic acid as a pale yellow solid (0.670 g, 16.6 mmol, 44%), mp 78−80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.94 (br s, 1H), 6.93−6.82 (m, 1H), 6.03−5.97 (m, 1H), 2.90−2.75 (m, 2H), 2.32 (d, J = 16.5, 2H), 1.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.0, 181.4, 148.0, 129.6, 46.9, 44.7, 35.3, 24.8. IR (neat): 2974, 1770. HRMS: exact mass calcd for $C_8H_{10}O_3$ $[M + H]^+$ 155.0708, found 155.0702.

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5-(((Cyclohexylideneamino)oxy)carbonyl)-5-methylcyclohex-2-enone (14). To a chilled solution (0 °C) of 1-methyl-5-oxocyclohex-3-enecarboxylic acid (0.30 g, 2.0 mmol, 1 equiv), cyclohexanone oxime (0.31 g, 2.7 mmol, 1.4 equiv), and *N*,*N*-dimethyl-4-aminopyridine (24 mg, 0.20 mmol 0.1 equiv) in DCM (30 mL) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (0.42 g, 2.7 mmol, 1.4 equiv), and the reaction mixture was stirred for 1 h at 0 °C. After warming to rt and stirring for 2 h, the reaction mixture was washed with saturated $NaHCO_3$ (2 × 30 mL), H_2O (1 × 30 mL), and brine (1 × 30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to leave a crude yellow oil that was purified by flash chromatography (silica gel 4:1 = Hex/EtOAc) to yield 5-(((cyclohexylideneamino)oxy)carbonyl)-5-methylcyclohex-2-enone as a white solid (0.36 g, 1.4 mmol, 74% yield), mp 47−49 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92−6.84 (m, 1H), 6.01 (dt, J = 9.9 and 2.1 Hz, 1H), 3.00−2.83 (m, 2H), 2.48−2.27 (m, 6H), 1.75−1.52 (m, 6H), 1.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.0, 172.9, 170.1, 147.5, 129.6, 46.9, 44.9, 35.9, 32.1, 27.1, 26.7, 25.8, 25.4, 25.0. IR (neat): 2933, 2859, 1743. HRMS: exact mass calcd for $C_{14}H_{19}NO_3$ $[M + H]^+$ 250.1438, found 250.1436.

■ ASSOCIATED CONTENT

Supporting Information

Film UV exposure studies and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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