mL) were heated to ca. 90 °C. Cholesteryl chloroformate (3.6 g, 8.0 mmol) was added, and the temperature was maintained at ca. 90 °C for 48 h. The mixture was cooled to room temperature, filtered, and concentrated in vacuo. Column chromatography (silica gel, 5% EtOAc/$CHCl_3$) followed by recrystallization (absolute EtOH) afforded pure **9** (2.75 g, 52%) of a white solid (mp 82–84 °C): ^{1}H NMR ($CDCl_3$) 1.50 (m, 44 H, steroid), 3.63 (m, 24 H, OCH_2CH_2O and CH_2NCH_2), 5.30 (dd, 1 H, C=CH); IR (KBr) 2940, 1705, 1470, 1380, 1160, 1130 cm^{-1}. Anal. Calcd for $C_{40}H_{69}NO_7$: C, 71.09; H, 10.29; N, 2.07. Found: C, 70.97; H, 10.20; N, 2.14.

X-ray Experimental. The structure of **8** was solved with data collected with Cu Kα radiation on a Nicolet P3/F diffractometer, by employing the SHELXTL system.[19] The orientation of the steroid ring system was determined by using the direct methods program SOLV, and its position relative to the symmetry axis was determined by translational search. Refinement was carried out with data collected on an Enraf-Nonius CAD4 diffractometer with Cu Kα radiation. Crystal data: $C_{38}H_{65}NO_6$, MW 631.9, monoclinic space group $P2_1$, $Z = 2$, $a = 12.293$ (2) Å, $b = 9.027$ (4) Å, $c = 16.858$ (2) Å, $\beta = 92.34$ (1)°, $V = 1869.2$ (14) Å^3, $D_c = 1.123$ g cm^{-3}, $\lambda =$ 1.54184 Å, $\mu = 5.53$ cm^{-1}, $T = 24$ °C. Data were collected by ω–2θ scans of speeds varying 0.83–4.0 deg min^{-1}. One quadrant of data within $2° < \theta < 75°$ yielded 4100 unique reflections, of which 2676 were considered observed, having $I > 1\sigma(I)$. Data reduction included corrections for background, Lorentz, polarization, and absorption by μ scans. The absolute configuration was assumed to correspond to that determined for other cholestanes.[15] Refinement was carried out by full-matrix least squares based on F with weights $w = \sigma^{-2}(F_o)$. Except for the disordered region, non-hydrogen atoms were refined anisotropically, and H atoms were placed in calculated positions. The three disordered atoms were assigned population = $^1/_2$ in six sites and refined isotropically, with H atoms ignored. Final $R = 0.074$ for 402 variables, with maximum electron density 0.22 e Å^3. Coordinates are listed in Table III; coordinates for hydrogen atoms and anisotropic thermal parameters are given in the supplementary material.

(19) Sheldrick, G. M. "*SHELTX User's Manual*, Nicolet: Madison, WI, 1983; Version 4.0.

Acknowledgment. We warmly thank the National Institutes of Health (GM-29150, GM-31846, GM-36262) and W. R. Grace & Co. Inc. for their support of this work.

Supplementary Material Available: Anisotropic thermal parameters and coordinates for hydrogen atoms in $C_{38}H_{65}NO_6$ (3 pages). Ordering information is given on any current masthead page.

2,4-Cyclohexadien-1-ones in Organic Synthesis. Further Studies of Molecular Rearrangements Occurring from Products of Intramolecular Azide–Olefin Cycloadditions

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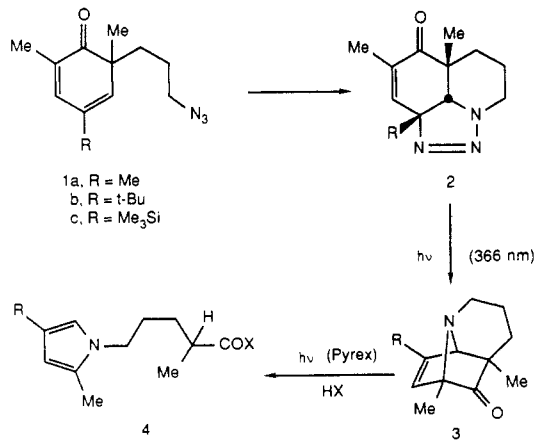
Thermolyses of 6-(3-azidopropyl)-2,4-cyclohexadien-1-ones **7a** and **7b** provide triazolines **8a** and **8b**, respectively. Photolysis of **8b** (366 nm) in methanol solution gives 2-azatricyclo[4.4.0.0^{2,8}]dec-9-en-7-one **9**, but photolysis of **8a** gives the pyrrole malonic ester **10a**. The inability to isolate the corresponding azatricycle **11** is explained by the operation of a retro-Mannich reaction of **11** to give zwitterion **12**, from which fragmentation occurs to give pyrrole ketene **13**. Reaction of **13** with methanol generates pyrrole malonic ester **10a**. Photolysis of **7a** (366 nm) in methanol solution gives azido diene **15**; thermolysis of **15** at 80 °C gives a mixture of diastereomeric vinylaziridines **16**. Acid-catalyzed rearrangement of **16** gives the butadiene carboxylic ester **17**, while thermolysis of **16** at 80–140 °C provides vinylogous urethane **20**. The rearrangement of **16** to **20** is suggested to occur by zwitterionization of **16** to give carbonyl-stabilized azomethine ylide **19**, followed by hydrogen atom rearrangement. Cycloadduct **21** is obtained on thermolysis of **16** in the presence of excess dimethyl acetylenedicarboxylate (DMAD). Vinylaziridine **23** (obtained from 2,4-cyclohexadienone **7b** via azido diene **22**) is stable to *p*-toluenesulfonic acid in THF at room temperature and attempted thermolysis at 140 °C.

Triazolines **2a–c** formed by intramolecular cycloaddition of 6-(3-azidopropyl)-2,4-cyclohexadien-1-ones **1a–c** photorearrange to 2-azatricyclo[4.4.0.0^{2,8}]dec-9-en-7-ones **3a–c** (Scheme I).[1] Azatricycles **3a–c** are photostable at 366 nm but undergo efficient photoconversion to pyrrole carboxylic acid derivatives **4a–c** on irradiation through Pyrex glassware. The fragmentation of **3a–c** presumably occurs by a photoinitiated retro-Diels–Alder reaction to give intermediate pyrrole ketenes (not shown), followed by addition of solvent (HX) to the ketene.

The sequence of reactions **1** → **2** → **3** provides a method for accomplishing the synthetic equivalence of an intramolecular cycloaddition between a diene and a nitrene. However, a limiting feature of the methodology is that the preparation of **1a–c** is based on C-alkylation of phenolic precursors. This procedure for construction of 2,4-cyclohexadienones requires the utilization of symmetrical 2,6-disubstituted phenols and only the most reactive alkylation

Scheme I



(1) (a) Schultz, A. G.; Dittami, J. P.; Myong, S. O.; Sha, C.-K. *J. Am. Chem. Soc.* **1983**, *105*, 3273. (b) Eng, K. K. Ph.D. Thesis, Rensselaer Polytechnic Institute, 1985.

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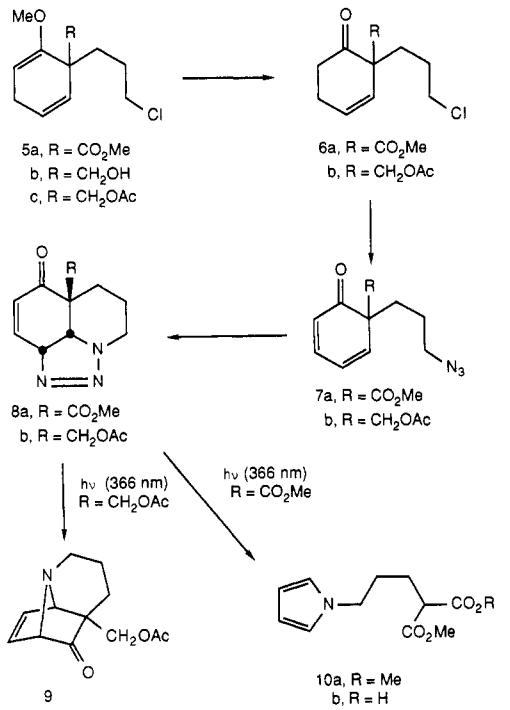
Scheme II



reagents. The Birch reductive alkylation of anisic acid derivatives has recently been used to construct a variety of 2,4-cyclohexadien-1-ones.[2] This development has provided a versatile new route to the 6-(3-azidopropyl)-2,4-cyclohexadien-1-ones **7**. In this paper, we report new chemistry encountered with **7a** and **7b**.

Results and Discussion

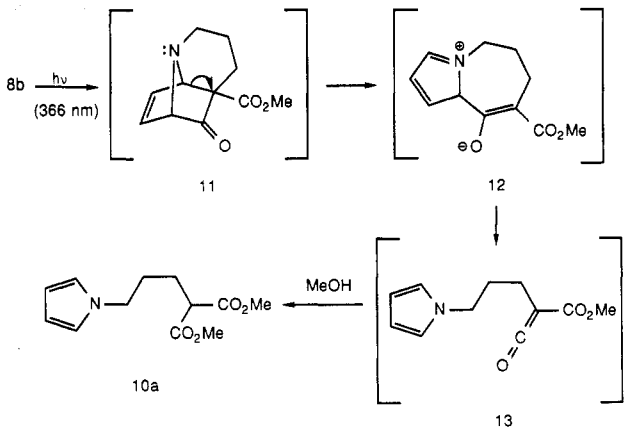
Triazoline Photorearrangements. The construction of 6-(3-azidopropyl)-6-carbomethoxy-2,4-cyclohexadien-1-one (**7a**) and 6-(acetoxymethyl)-6-(3-azidopropyl)-2,4-cyclohexadien-1-one (**7b**) is outlined in Scheme II and is described in detail in the Experimental Section. Thermolysis of **7a** in refluxing benzene solution provides triazoline **8a** in 61% isolated yield.[3]

Irradiation of **8a** with 366 nm light in reagent-grade methanol solution gives pyrrole malonic ester **10a** in quantitative yield rather than the expected azatricycle **11**. When the irradiation of **8a** was conducted in carefully dried methanol solution, a substance tentatively identified as **11** along with pyrrole malonic ester **10a** was observed by ^{1}H NMR spectroscopy. This new substance could not be isolated but was converted to the pyrrole carboxylic acid **10b** on attempted chromatography on silica gel.

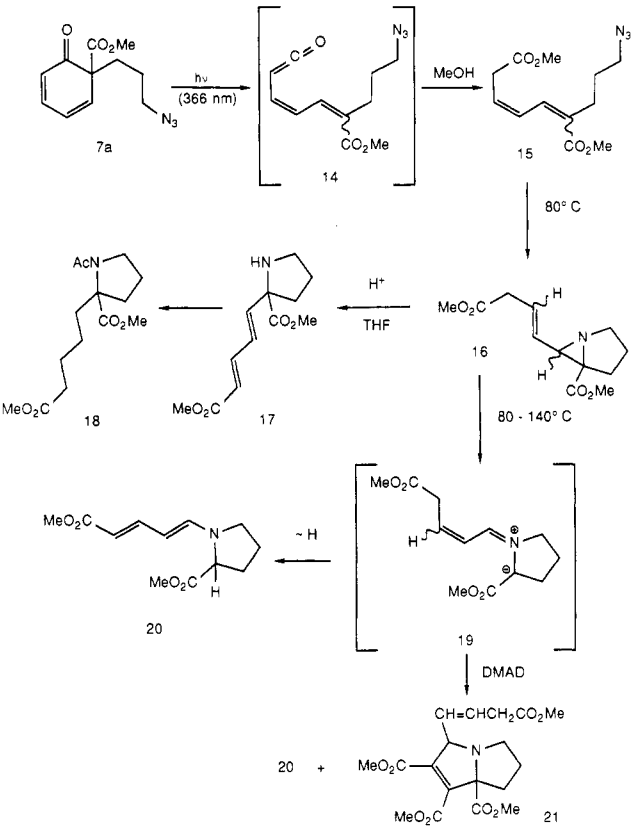
The inability to isolate **11** from preparative photoreactions of **8a** probably is a result of decreased chemical stability of **11** relative to the series **3a–c**. The instability of **11** may be a result of the opportunity for a facile retro-Mannich reaction[4] which would give zwitterion **12** (Scheme III). Fragmentation of **12** would generate pyrrole ketene **13**, the presumed precursor of pyrrole malonic ester **10a** and the carboxylic acid analogue **10b**.

On the basis of the rationale presented in Scheme III, we expected that substitution of an acetoxymethyl group for the carbomethoxy group in **11** would provide a measure of stability toward the retro-Mannich process. Triazolene **8b** was prepared and irradiation at 366 nm in methanol

Scheme III



Scheme IV



solution gave azatricyclodecenone **9** in 63% isolated yield (Scheme II). Significantly, ^{1}H NMR resonances for **9** in the olefinic region are nearly identical with those observed for the unstable reaction intermediate **11**.

The retro-Mannich process is disfavored in **9** because of an improper orientation of orbitals in the C–C bond that would undergo fragmentation with respect to the p-orbitals of the ketone carbonyl group. The carbomethoxy group in **11** apparently can adopt a conformation with a proper orientation of orbitals for the C–C bond fragmentation.[5]

Vinylaziridine Rearrangements. Ultraviolet irradiation of 2,4-cyclohexadien-1-ones in the presence of appropriate nucleophilic solvents produces diene carboxylic acid derivatives in high yield.[6] We have been interested in the utilization of this process in organic synthesis[7] and,

(2) Schultz, A. G.; Dittami, J. P.; Lavieri, F. P.; Salowey, C.; Sundararaman, P.; Szymula, M. B. *J. Org. Chem.* **1984**, *49*, 4429.
(3) For a discussion of the assignment of relative configuration in triazolines related to **8a** and **8b**, see ref 1.
(4) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 535.
(5) For another substituent effect on the stability of a 2-azatricyclodecenone, see the discussion concerning the conversion of **17a** to **18** in ref 1a.
(6) Barton, D. H. R.; Quinkert, G. *J. Chem. Soc.* **1960**, 1.

for this reason, examined the photoreactivity of **7a** and **7b** in methanol solution. Irradiation of **7a** in dry methanol for 1.5 h gives **15** as a 2:1 mixture of C(5)–C(6) olefin isomers in 98% isolated yield (Scheme IV), presumably via diene ketene **14**.[8] Similarly, **7b** is converted to a 1.2:1 mixture of isomers **22** in 87% yield.

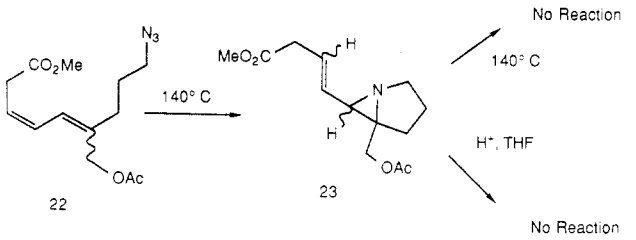
It is noteworthy that the photorearrangement of the 2,4-cyclohexadienone unit in **7a** and **7b** occurs efficiently in the presence of the potentially photoreactive azide group. This chemoselectivity is explained by selective irradiation of the long wavelength UV absorption band of the dienone chromophore in a spectral region (366 nm) for which the azide group is nonabsorbent. This same kind of chemoselectivity had been demonstrated earlier in the context of 4-(azidoalkyl)-2,5-cyclohexadien-1-one photochemistry.[9]

Thermolysis of azido diene **15** in refluxing benzene solution, to the point of complete disappearance of **15**, gives rise to vinylaziridine **16** (61%; mixture of diastereoisomers) and vinylogous urethane **20** (28%). In a separate experiment, it was shown that aziridine **16** undergoes clean rearrangement to **20** in refluxing xylenes (~140 °C).

The rearrangement of **16** to **20** is thought to occur by zwitterionization of **16** to give carbonyl-stabilized azomethine ylide **19**.[10] Hydrogen atom transfer to give **20** could occur by a [1,6] sigmatropic rearrangement (formally analogous to a [1,7] sigmatropic hydrogen shift in the hepatrienyl series);[11] however, other bimolecular reaction mechanisms are certainly possible. That ylide **19** is to be considered a viable intermediate in the production of **20** was demonstrated by thermolysis of **16** in refluxing xylene solution in the presence of excess dimethyl acetylenedicarboxylate (DMAD).[12] Under these conditions, a reduced quantity of **20** was generated (38%), together with cycloadduct **21**. The reaction mixture was separated by chromatography on silica gel, and **21** was obtained in 45% yield as an inseparable mixture of diastereoisomers.

Another potentially useful rearrangement was encountered on treatment of aziridine **16** with *p*-toluenesulfonic acid in THF at room temperature. Filtration of the reaction mixture through silica gel provided *trans,trans*-butadiene carboxylic ester **17** in 98% yield. Characterization of this substance consisted of the usual analytical and spectroscopic methods along with hydrogenation and subsequent acetylation to give the saturated diester amide **18** in an almost quantitative yield.

We were particularly interested in the role of the angular carbomethoxy group in **16** in rearrangement to **17** and **20**. Consequently, azido diene **22** was prepared by photolysis of **7b**, and aziridine **23** was obtained by thermolysis of **22** in refluxing xylenes. In contrast to the thermal behavior of **16**, vinylaziridine **23** did not undergo rearrangement to the analogue of vinylogous urethane **20**. This observation is consistent with the expected stabilizing effect of the carbomethoxy group on azomethine ylide **19**.[10] Treatment



of **23** with *p*-toluenesulfonic acid using conditions that promoted the rearrangement of **16** to **17** had no effect on **23**. Except for some uncharacterized decomposition, vinylaziridine **23** was recovered unchanged.

Conclusion

6-(3-Azidopropyl)-2,4-cyclohexadien-1-ones of type **7** are easily prepared and undergo conversions to a variety of highly functionalized nitrogen-containing ring systems. This methodology is expected to be useful in the development of new routes to pyrrolizidines, indolizidines, and other natural products.

Experimental Section

^{1}H NMR spectra were recorded on Varian XL-200 (200 MHz), IBM WP-100SY (100 MHz), and Hitachi-Perkin-Elmer R-600 (60 MHz) NMR spectrometers (tetramethylsilane internal standard). ^{13}C NMR spectra were obtained on the Varian XL-200 and IBM WP-100SY spectrometers. Infrared spectra were obtained on a Perkin-Elmer 298 spectrometer, and ultraviolet spectra were recorded on a Perkin-Elmer 552 spectrometer. Mass spectra were obtained on a Hewlett-Packard 5987A GC–MS system (methane, chemical ionization gas). Elemental analyses were determined by Spang Microanalytical Laboratories, Eagle Harbor, MI. The light source for all photochemistry was a Hanovia 450-W medium-pressure mercury arc lamp. The lamp was placed in a water-cooled Pyrex immersion well. Reaction vessels containing solutions to be irradiated were attached to the immersion well and were saturated with nitrogen prior to irradiation. The Hanovia lamp in the Pyrex immersion well fitted with Corning color filters 0-25 and 7-54 was employed as the 366-nm light source. Purifications by flash chromatography used either Baker silica gel with a 40 μm average particle diameter or Baker neutral alumina with a 50–200 μm average particle diameter.

6-Hydroxymethyl-6-(3-chloropropyl)-1-methoxy-1,4-cyclohexadiene (5b). To a stirred suspension of lithium aluminum hydride (0.321 g, 8.45 mmol) in dry THF (20 mL) at room temperature was added a solution of 6-carbomethoxy-6-(3-chloropropyl)-1-methoxy-1,4-cyclohexadiene (**5a**, 1.013 g, 4.15 mmol)[2] in dry THF (5 mL). The reaction mixture was warmed to 50 °C for 1 h, cooled to 0 °C, and carefully quenched with a saturated aqueous solution of sodium sulfate. The insoluble salts were removed by filtration. Removal of the solvent gave crude **5b** (0.753 g, 84%), which was used without further purification: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.60–1.88 (4 H, m), 2.82 (2 H, m), 3.28–3.72 (2 H, m), 3.50 (2 H, dt, J = 6.6, 2.1 Hz), 3.55 (3 H, s), 4.88 (1 H, t, J = 3.3 Hz), 5.26 (1 H, dt, J = 9.9, 2.0 Hz), 5.98 (1 H, dt, J = 9.9, 2.2 Hz); IR (film) 3400 (br), 1675, 1640 cm^{-1}; mass spectrum (CI), m/z 217 (M^+ + 1), 199, 181, 157, 121.

6-(Acetoxymethyl)-6-(3-chloropropyl)-1-methoxy-1,4-cyclohexadiene (5c). To a solution of alcohol **5b** (0.753 g, 3.49 mmol) in pyridine (10 mL) was added acetic anhydride (1.81 g, 17.7 mmol) and a catalytic amount of 4-(dimethylamino)pyridine. After 4 h at room temperature, the reaction mixture was concentrated under reduced pressure. The product was purified by flash chromatography (silica gel; ethyl acetate/hexanes, 1:2) to give **5c** (0.786 g, 87%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26–1.79 (4 H, m), 2.01 (3 H, s), 2.77 (2 H, m), 3.46–3.53 (2 H, m), 3.51 (3 H, s), 4.08 (2 H, m), 4.80 (1 H, t, J = 3.4 Hz), 5.33 (1 H, dt, J = 10.0, 2.1 Hz), 5.87 (1 H, dt, J = 10.0, 2.2 Hz); IR (film) 1730, 1680, 1645 cm^{-1}; mass spectrum (CI), m/z 259 (M^+ + 1), 199, 163, 121.

Anal. Calcd for $C_{13}H_{19}ClO_3$: C, 60.35; H, 7.40. Found: C, 60.42; H, 7.38.

6-(Acetoxymethyl)-6-(3-chloropropyl)-3-cyclohexen-1-one (6b). A solution of **5c** (0.770 g, 2.98 mmol) in 10% methanolic

(7) Schultz, A. G.; Kulkarni, Y. S. *J. Org. Chem.* **1984**, *49*, 5202.
(8) (a) Quinkert, G. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 211. (b) Quinkert, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1072. (c) Quinkert, G. *Pure Appl. Chem.* **1973**, *33*, 285. (d) Quinkert, G.; Billhardt, V.-M.; Paulus, E. F.; Bats, J. W.; Fuess, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 442.
(9) Schultz, A. G.; Myong, S. O.; Puig, S. *Tetrahedron Lett.* **1984**, *25*, 1011.
(10) For a recent discussion of the thermal conversion of aziridines to azomethine ylides, see: Lown, J. W. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; p 653.
(11) Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1970; Chapter 7.
(12) (a) Heine, H. W.; Peavy, R. *Tetrahedron Lett.* **1965**, 3123. (b) Huisgen, R.; Scheer, W.; Mader, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 604.

HCl (30 mL) was stirred at room temperature for 5 h. The reaction mixture was neutralized ($NaHCO_3$), and the solvent was partially removed under reduced pressure. The residue was poured into brine, diluted with H_2O (10 mL), and extracted with methylene chloride (3 × 20 mL). The combined extracts were washed with water and brine, dried (Na_2SO_4), and concentrated. ^1H NMR and IR of the crude product indicated the presence of both **6b** and a small amount of the 6-hydroxymethyl derivative. The mixture was dissolved in pyridine (5 mL), and acetic anhydride (1 mL) was added. After being stirred at room temperature overnight the reaction mixture was concentrated under reduced pressure. The product was purified by flash chromatography (silica gel; ethyl acetate/hexanes, 1:2) to give **6b** (0.580 g, 80%): ^1H NMR (200 MHz, $CDCl_3$) δ 1.45–2.00 (4 H, m), 2.02 (3 H, s), 2.42–2.56 (4 H, m), 3.48 (2 H, m), 4.11 (2 H, m), 5.51 (1 H, m), 6.12 (1 H, m); IR (film) 1730, 1705 cm^{-1}; mass spectrum (CI), m/z 245 ($M^+ + 1$), 209, 185, 149.

Anal. Calcd for $C_{12}H_{17}ClO_3$: C, 58.90; H, 7.00. Found: C, 59.03; H, 7.03.

6-(Acetoxymethyl)-6-(3-chloropropyl)-2,4-cyclohexadien-1-one. A solution of **6b** (0.168 g, 0.689 mmol) and *N*-bromosuccinimide (0.132 g, 0.742 mmol) in dry benzene (10 mL) was heated to reflux temperature and irradiated with a sun lamp for 1.3 h. The reaction mixture was washed sequentially with saturated sodium thiosulfate solution (10 mL), water (10 mL), and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The product was purified by flash chromatography (silica gel; ethyl acetate/hexanes, 1:3) to give 0.103 g (62%) of product: ^1H NMR (200 MHz, $CDCl_3$) δ 1.55–1.99 (4 H, m), 1.96 (3 H, s), 3.43 (2 H, m), 4.26 (2 H, m), 6.01 (1 H, m), 6.32 (1 H, m), 6.43 (1 H, m), 7.07 (1 H, m); IR (film) 1730, 1655, 1625 cm^{-1}; mass spectrum (CI), m/z 243 ($M^+ + 1$), 213, 183, 147.

Anal. Calcd for $C_{12}H_{15}ClO_3$: C, 59.39; H, 6.23. Found: C, 59.21; H, 6.22.

6-(3-Azidopropyl)-6-carbomethoxy-2,4-cyclohexadien-1-one (7a). To a solution of 6-carbomethoxy-6-(3-chloropropyl)-2,4-cyclohexadien-1-one (1.6 g, 7.0 mmol)[2] in dry DMF (14 mL) was added tetramethylammonium iodide (2.9 g, 14 mmol) followed by sodium azide (0.9 g, 16 mmol). The mixture was stirred at 50 °C for 24 h. The solvent was removed under reduced pressure, and the residue was partitioned between ether (30 mL) and water (15 mL). The aqueous layer was extracted with ether (20 mL). The combined organic layers were washed successively with water (2 × 10 mL) and brine (2 × 10 mL) and dried (Na_2SO_4). The product was purified by flash chromatography (silica gel; hexanes/ethyl acetate, 4:1) to afford **7a** (0.55 g, 33%): ^1H NMR (200 MHz, $CDCl_3$) δ 1.3–1.6 (2 H, m), 1.96–2.12 (1 H, m), 2.24–2.41 (1 H, m), 3.25 (2 H, m), 3.69 (3 H, s), 6.12 (1 H, d, J = 10 Hz), 6.29 (1 H, br d, J = 10 Hz), 6.45 (1 H, dd, J = 9, 2 Hz), 7.11 (1 H, ddd, J = 9, 6, 2 Hz); ^{13}C NMR ($CDCl_3$) 23.45, 34.03, 51.28, 53.01, 62.27, 123.54, 126.55, 139.35, 141.48, 169.22, 197.73; IR (film) 2950, 2100, 1739, 1665, 1630, 1560, 1440, 1230, 1135 cm^{-1}; mass spectrum (CI), m/z 236 ($M^+ + 1$), 208 ($-N_2$), 193, 177, 153, 149.

6a-Carbomethoxy-5,6,6a,7,9a,9b-hexahydro-7-oxo-4*H*-1,2,3-triazolo[4,5,1-*ij*]quinoline (8a). A solution of azide **7a** (0.325 g, 1.38 mmol) in dry benzene (30 mL) was heated at reflux temperature for 12 h. The solvent was removed under reduced pressure, and the product was purified by flash chromatography (silica gel; hexanes/ethyl acetate, 1:1) to afford **8a** (0.196 g, 61%): ^1H NMR (200 MHz, $CDCl_3$) δ 1.41–1.85 (3 H, m), 2.94–3.18 (2 H, m), 3.57 (1 H, d, J = 10 Hz), 3.73 (3 H, s), 4.32 (1 H, br d, J = 12 Hz), 5.31 (1 H, br d, J = 10 Hz), 6.17 (1 H, dd, J = 9.5, 2 Hz), 6.45 (1 H, dd, J = 9.5, 4 Hz); ^{13}C NMR ($CDCl_3$) δ 21.41, 28.85, 46.76, 53.18, 55.20, 59.55, 71.47, 129.91, 136.48, 169.39, 190.72; IR (film) 1730, 1680 cm^{-1}; mass spectrum (CI), m/z 236 ($M^+ + 1$), 208 ($-N_2$), 176, 148; UV (MeOH) λ_{max} (ε) 223 nm (9930), 252 (6470) with tailing to 400 nm.

Anal. Calcd for $C_{11}H_{13}N_3O_3$: C, 56.16; H, 5.57; N, 17.86. Found: C, 56.11; N, 5.57; N, 17.78.

Photolysis of Triazoline 8a. Method 1: Preparation of Pyrrole Diester 10a. A solution of **8a** (25 mg, 0.11 mmol) in spectrophotometric grade methanol (10 mL) was irradiated through Pyrex glass for 0.5 h. The solvent was removed under reduced pressure, and the product was purified by flash chromatography (silica gel; ethyl acetate/hexanes, 1:2) to give **10a** (23 mg, 85%): ^1H NMR (200 MHz, $CDCl_3$) δ 1.72–2.05 (4 H, m), 3.36 (1 H, t, J = 8 Hz), 3.73 (6 H, s), 3.92 (2 H, t, J = 8 Hz), 6.16 (2 H, t, J = 2 Hz), 6.66 (2 H, t, J = 2 Hz); IR (film) 1740 cm^{-1}; mass spectrum (CI), m/z 240 ($M^+ + 1$).

Method 2: ^1H NMR Observation of Azatricyclodecenone 11. A solution of **8a** (24.3 mg, 0.103 mmol in dry methanol (10 mL) was saturated with dry nitrogen and irradiated at 366 nm for 0.5 h. Removal of solvent gave a residue which by ^1H NMR analysis (200 MHz, $CDCl_3$) appeared to consist of a mixture of starting material, pyrrole diester **10a**, and a third compound in the approximate ratio of 1:2:2, respectively. The ^1H NMR spectrum (200 MHz) of this third component possessed resonances (δ 6.36 and 6.84) in the same region and with the same multiplicities as azatricyclodecenone **9**. However, upon flash chromatography (silica gel; ethyl acetate/hexanes, 1:1) of the mixture, only pyrrole diester **10a** (6.0 mg, 24%), pyrrole acid **10b** (7.7 mg, 33%), and starting material **8a** (5.1 mg, 21%) were obtained.

Pyrrole Carboxylic Acid 10b. A solution of **8a** (15 mg, 0.064 mmol) in dry THF (6 mL, 0.01 M) was saturated with dry nitrogen and irradiated at 366 nm for 2.5 h. The solvent was removed; flash chromatography of the residue (silica gel; ethyl acetate/methanol, 9:1) gave **10b** (11 mg, 77%): ^1H NMR (200 MHz, $CDCl_3$) δ 1.85 (4 H, m), 3.34 (1 H, t, J = 6.0 Hz), 3.73 (3 H, s), 3.89 (2 H, t, J = 6.8 Hz), 4.8 (1 H, br s), 6.12 (1 H, t, J = 2.1 Hz), 6.63 (1 H, t, J = 2.1 Hz); IR (film) 3700–2300 (br), 1715 (br) cm^{-1}; mass spectrum (CI), m/z 226 ($M^+ + 1$), 182, 150.

6-(Acetoxymethyl)-6-(3-azidopropyl)-2,4-cyclohexadien-1-one (7b) and 6a-Acetoxy-5,6,6a,7,9a,9b-hexahydro-7-oxo-4*H*-1,2,3-triazolo[4,5,1-*ij*]quinoline (8b). To a solution of 6-(acetoxymethyl)-6-(3-chloropropyl)-2,4-cyclohexadien-1-one (0.103 g, 0.426 mmol) in reagent grade acetone (5 mL) was added a saturated solution of sodium iodide in acetone (20 mL). The mixture was refluxed overnight and partitioned between water (20 mL) and ether (20 mL). The ether layer was separated, and the aqueous phase was extracted once with ether (10 mL). The ether extracts were combined, washed sequentially with saturated aqueous sodium thiosulfate solution (10 mL), water, and brine, dried (Na_2SO_4), and evaporated under reduced pressure to give crude 6-(acetoxymethyl)-6-(3-iodopropyl)-2,4-cyclohexadien-1-one (0.120 g, 84%): ^1H NMR (200 MHz, $CDCl_3$) δ 1.58–1.99 (4 H, m), 1.96 (3 H, s), 3.06 (2 H, m), 4.25 (2 H, m), 6.11 (1 H, m), 6.31 (1 H, m), 6.42 (1 H, m), 7.08 (1 H, m); IR (film) 1730, 1655, 1630 cm^{-1}; mass spectrum (CI), m/z 335 ($M^+ + 1$), 305, 275, 177, 147.

The crude iodide (0.105 g, 0.314 mmol) was treated with sodium azide (65 mg, 1.0 mmol) in dry DMF (5 mL), and the mixture was heated at 50 °C for 3 h. The solvent was removed under reduced pressure, the resulting brown sludge was suspended in ether (20 mL), the insoluble material was removed by filtration through a pad of Celite, and the filtrate was concentrated. The products were separated by flash chromatography (silica gel; ethyl acetate/hexanes, 1:3) to give azide **7b** (30.0 mg, 38%) and triazoline **8b** (31.7 mg, 41%).

7b: ^1H NMR (200 MHz, $CDCl_3$) δ 1.28–1.95 (4 H, m), 1.98 (3 H, s), 3.19 (2 H, m), 4.22 (2 H, m), 6.12 (1 H, m), 6.31 (1 H, m), 6.44 (1 H, m), 7.10 (1 H, m); IR (film) 2090, 1735, 1655, 1630 cm^{-1}; mass spectrum (CI), m/z 250 ($M^+ + 1$), 190, 150.

Anal. Calcd for $C_{12}H_{15}N_3O_3$ (**7b**): C, 57.82; H, 6.07. Found: C, 57.64; H, 6.10.

8b: ^1H NMR (200 MHz, $CDCl_3$) δ 1.41–1.79 (4 H, m), 2.01 (3 H, s), 3.12 (2 H, m), 4.05 (2 H, m), 4.31 (1 H, m), 5.10 (1 H, m), 6.19 (1 H, m), 6.49 (1 H, m); IR (film) 1675 cm^{-1}; mass spectrum (CI), m/z 250 ($M^+ + 1$), 222, 190, 162, 150.

6-(Acetoxymethyl)-2-azatricyclo[4.4.0.0^{2,8}]dec-9-en-7-one (9). A solution of **8b** (9.5 mg, 0.038 mmol) in dry methanol (3.5 mL, 0.01 M) was saturated with dry nitrogen and irradiated at 366 nm for 1 h. After removal of solvent the product was purified by preparative TLC (silica gel, 20 × 20 cm plate; ethyl acetate/methanol, 9:1) to give **9** (5.3 mg, 63%): ^1H NMR (200 MHz, $CDCl_3$) δ 1.4–2.4 (4 H, m), 2.05 (3 H, s), 3.1 (2 H, m), 3.6–4.0 (2 H, m), 3.95 (2 H, m), 6.35 (1 H, m), 6.73 (1 H, m); IR (film) 1730 (br) cm^{-1}; mass spectrum (CI), m/z 222 ($M^+ + 1$), 162, 133.

An acceptable elemental analysis could not be obtained for this compound.

Methyl 9-Azido-6-carbomethoxy-3,5-nonadienoate (15). A solution of **7a** (0.112 g, 0.477 mmol) in dry methanol (2 mL) was saturated with dry nitrogen and irradiated at 366 nm for 1.5 h. The solvent was removed under reduced pressure, and the product

was purified by flash chromatography (silica gel, ethyl acetate/hexanes, 1:3) to give **15** (0.124 g, 98%) as an inseparable mixture of isomers (2:1): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.68–1.86 (2 H, m), 2.40–2.60 (2 H, m), 3.24–3.46 (4 H, m), 3.64 (3 H, s), 3.70 (3 H, s), 5.88–6.36 (1 H, m), 6.46–6.74 (1 H, m), 7.05–7.50 (1 H, m); IR (film) 1730, 1705 cm^{-1}; mass spectrum (CI), m/z 268 (M^+ + 1), 240, 208, 180, 148.

Anal. Calcd for $C_{12}H_{17}N_3O_4$: C, 53.92; H, 6.41. Found: C, 54.00; H, 6.32.

Thermolysis of 15. Method 1: Preparation of Vinylaziridine 16. A solution of **15** (83.5 mg, 0.313 mmol) in dry benzene (5 mL) was heated to reflux temperature for 18 h. The solvent was removed under reduced pressure, and the product was purified by flash chromatography on silica gel using gradient elution with ethyl acetate/hexanes (1:1) followed by ethyl acetate to give **16** (45.5 mg, 61%) as an inseparable mixture of isomers along with **20** (21 mg, 28%). **16**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.4–1.7 (1 H, m), 1.8–2.3 (2 H, m), 2.45 (1 H, m), 2.78 (1 H, m), 3.0–3.4 (4 H, m), 3.69 (3 H, s), 3.72 (3 H, s), 5.3–5.7 (1 H, m), 5.7–6.2 (1 H, m); IR (film) 1720 cm^{-1}; mass spectrum (CI), m/z 240 (M^+ + 1), 208, 180.

Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16. Found: C, 60.26; H, 7.20.

Method 2: Preparation of Vinylogous Urethane 20. A solution of isomeric azides **15** (0.139 g, 0.521 mmol) in xylenes (20 mL) was heated to reflux temperature for 18 h. The solvent was removed under reduced pressure, and the product was purified by flash chromatography (silica gel; ethyl acetate/hexanes, 1:1) to give **20** (70 mg, 56%) along with isomeric vinylaziridines **16** (15 mg, 12%). **20**: mp 106–109 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.02–2.22 (4 H, m), 3.31 (2 H, m), 3.69 (3 H, s), 3.75 (3 H, s), 4.12 (1 H, dd, J = 4.0, 7.8 Hz), 5.12 (1 H, dt, J = 11.7, 12.7 Hz), 5.49 (1 H, d, J = 14.9 Hz), 6.80 (1 H, d, J = 13 Hz), 7.30 (1 H, dd, J = 3.3, 11.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8, 30.1, 48.8, 50.8, 52.4, 62.3, 98.8, 108.2, 145.2, 147.1, 169.0, 180.5; IR ($CDCl_3$) 1725, 1680, 1590 cm^{-1}; mass spectrum (CI), m/z 240 (M^+ + 1), 208, 180.

Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16. Found: C, 60.25; H, 7.20.

Thermolysis of 16. A solution of isomeric vinylaziridines **16** (20 mg, 0.084 mmol) in xylenes (5 mL) was heated to reflux temperature for 3 h. Evaporation of solvent afforded **20** (18 mg, 90%).

Butadiene Carboxylic Ester 17. A solution of isomeric vinylaziridines **16** (15.2 mg, 0.0636 mmol) in dry THF (2 mL) was treated with a catalytic amount of *p*-toluenesulfonic acid overnight. The reaction mixture was passed through a pad of silica gel and evaporation of solvent afforded **17** (15 mg, 98%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.58–2.49 (4 H, m), 2.60 (1 H, br m), 3.09 (2 H, m), 3.74 (3 H, s), 3.76 (3 H, s), 5.90 (1 H, d, J = 15.5 Hz), 6.30 (1 H, d, J = 15.0 Hz), 6.53 (1 H, dd, J = 10.9, 5.1 Hz), 7.30 (1 H, dd, J = 10.8, 15.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 37.1, 46.5, 51.5, 52.8, 70.3, 121.3, 127.2, 143.9, 144.2, 167.3, 175.2; IR (film) 1710 (br), 1635 cm^{-1}; mass spectrum (CI) m/z 240 (M^+ + 1), 208, 180, 166.

Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16. Found: C, 60.31; H, 7.16.

Saturated Diester Amide 18. To a solution of **17** (10.2 mg, 0.0427 mmol) in 5% methanolic HCl (10 mL) was added 15 mg of 10% palladium on carbon. The mixture was subjected to 1 atm of hydrogen overnight, the catalyst was removed by filtration through Celite, and the filtrate was neutralized with saturated aqueous sodium bicarbonate. The mixture was extracted with ethyl acetate (3 × 10 mL), and the organic extracts were combined, washed with water and brine, and dried ($MgSO_4$). Evaporation of solvent under reduced pressure afforded the desired saturated diester amine (10.2 mg, 98%), which was used without further purification: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9–2.0 (10 H, m), 2.26 (2 H, t, J = 7 Hz), 2.85 (1 H, br s), 2.96 (2 H, t, J = 6 Hz), 3.62 (3 H, s), 3.69 (3 H, s); IR (film) 1720 cm^{-1}; mass spectrum (CI), m/z 244 (M^+ + 1), 226, 184.

The crude amine (10.2 mg, 0.042 mmol) was dissolved in pyridine (1 mL), and acetic anhydride (0.5 mL) was added. The mixture was stirred for 4 h, and the solvents were removed under reduced pressure. The product was purified by flash chromatography (silica gel, ethyl acetate) to afford **18** (12 mg, 100%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.0–2.1 (12 H, m), 2.06 (3 H, s), 2.32 (2 H, t, J = 8 Hz), 3.67 (3 H, s), 3.70 (3 H, s); IR (film) 1725, 1635 cm^{-1}; mass spectrum (CI), m/z 286 (M^+ + 1), 254, 226, 212.

Anal. Calcd for $C_{14}H_{23}NO_5$: C, 58.93; H, 8.12. Found: C, 59.08; H, 8.25.

Cycloadduct 21. To a solution of isomeric aziridines **16** (22.9 mg, 0.0958 mmol) in xylenes (5 mL) was added dimethyl acetylenedicarboxylate (36.4 mg, 0.256 mmol). The mixture was heated to reflux temperature for 5 h, and the solvent was removed under reduced pressure. Flash chromatography of the residue (silica gel; gradient elution, ethyl acetate/hexanes, 1:1, to ethyl acetate) afforded **20** (8.7 mg, 38%) and **21** (16.6 mg, 45%) as a mixture of isomers: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.5–3.4 (8 H, m), 3.5–3.9 (12 H, overlapping s), 5.2 (1 H, m), 5.6 (1 H, m), 6.0 (1 H, m); IR (film) 1710 (br) cm^{-1}; mass spectrum (CI), m/z 382 (M^+ + 1), 350, 322, 250.

Methyl 6-(Acetoxymethyl)-9-azido-3,5-nonadienoate (22). A solution of **7b** (23.2 mg, 0.0932 mmol) in dry methanol (5 mL) was saturated with dry nitrogen and irradiated at 366 nm for 1.25 h. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica gel; ethyl acetate/hexanes, 1:3) to give **22** (22.9 g, 87%) as a 1.2:1 mixture of isomers: ^{1}H NMR ($CDCl_3$) δ 1.63–1.82 (2 H, m), 2.09 (minor isomer, 3 H, s), 2.11 (major isomer, 3 H), 2.25–2.35 (2 H, m), 3.25–3.35 (4 H, m), 3.72 (3 H, s), 4.60 (major isomer, 2 H, s), 4.73 (minor isomer, 2 H, s), 5.75 (1 H, m), 6.29–6.40 (2 H, m); IR (film) 2090, 1725 (br) cm^{-1}; mass spectrum (CI), m/z 282 (M^+ + 1), 254, 222, 194, 162.

Anal. Calcd for $C_{13}H_{19}N_3O_4$: C, 55.51; H, 6.81. Found: C, 55.84; H, 6.54.

Vinylaziridine 23. A solution of isomeric azides **22** (17.6 mg, 0.0626 mmol) in xylenes (3 mL) was heated to reflux temperature for 7 h. The solvent was removed under reduced pressure, and the product was purified by flash chromatography (silica gel; ethyl acetate) to give vinylaziridine **23** (12.5 mg, 79%) as a mixture of isomers: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.34–2.48 (4 H, m), 2.07 (3 H, s), 2.53–2.82 (1 H, m), 2.90–3.26 (4 H, m), 3.58 (3 H, s), 3.92–4.18 (2 H, m), 5.33–6.23 (2 H, m); IR (film) 1720 (br) cm^{-1}; mass spectrum (CI), m/z 254 (M^+ + 1), 236, 222, 194.

An acceptable elemental analysis could not be obtained for this compound.

Reaction of 23 with PTSA. To a solution of isomeric vinylaziridines **23** (10 mg, 0.040 mmol) in THF (1 mL) was added a catalytic amount of *p*-toluenesulfonic acid. The mixture was stirred at room temperature overnight, and the solvent was removed under reduced pressure. TLC and ^{1}H NMR (200 MHz, $CDCl_3$) analysis of the residue (10 mg) indicated the presence of unreacted **23** exclusively.

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Registry No. **5a**, 86990-71-8; **5b**, 108345-63-7; **5c**, 108345-64-8; **6b**, 108345-65-9; **7a**, 108345-66-0; **7b**, 108345-67-1; **8a**, 108345-68-2; **2b**, 108345-69-3; **9**, 108345-70-6; **10a**, 108345-71-7; **10b**, 108345-72-8; (*E*,*Z*)-**15**, 108345-73-9; (*Z*,*Z*)-**15**, 108345-74-0; **16**, 108345-75-1; **17**, 108345-76-2; **17**(saturated diester amine), 108345-77-3; **18**, 108345-78-4; **20**, 108345-79-5; **21**, 108365-61-3; (*Z*,*E*)-**22**, 108345-80-8; (*Z*,*Z*)-**22**, 108345-81-9; **23**, 108345-82-0; 6-(acetoxymethyl)-6-(3-chloropropyl)-2,4-cyclohexadien-1-one, 108345-83-1; 6-carbomethoxy-6-(3-chloropropyl)-2,4-cyclohexadien-1-one, 86990-79-6; 6-(acetoxymethyl)-6-(3-iodopropyl)-2,4-cyclohexadien-1-one, 108345-84-2; dimethyl acetylenedicarboxylate, 762-42-5.