DHV$_2$-II (5). UV (c 2.08 × 10^{-5} M, CH_3OH) λ_{260} (ϵ 23 560), $\lambda_{250.5}$ (ϵ 35 580), $\lambda_{242.5}$ (ϵ 30 770), and λ_{235} (ϵ 21 150); CD (c 6.92 × 10^{-5} M, CH_3OH) $[\theta]_{260}$ +5440, $[\theta]_{250}$ +6300, $[\theta]_{242}$ +5440, $[\theta]_{235}$ +12300, and $[\theta]_{216}$ +32600.

DHV$_2$-IV (6). UV (c 1.19 × 10^{-5} M, CH_3OH) $\lambda_{259.5}$ (ϵ 23 060), λ_{250} (ϵ 34 250), λ_{242} (ϵ 29 680), and λ_{235} (ϵ 21 230); CD (c 7.31 × 10^{-5} M, CH_3OH) $[\theta]_{260}$ −10 000, $[\theta]_{250}$ −15 400, $[\theta]_{242}$ −11 900, and $[\theta]_{218}$ +12 500.

Acknowledgment. We wish to thank Professor William H. Okamura for providing us with samples of the 10,19-dihydrovitamin D isomers used in this work.

Registry No. 3, 67-96-9; **4**, 65377-91-5; **5**, 65377-86-8; **6**, 807-27-2; **7**, 67-97-0; **8**, 66251-18-1; **8** DNP, 84928-42-7; **9**, 84943-83-9; **10**, 84928-43-8; **11**, 84928-44-9; **12**, 84928-45-0; **13**, 84928-46-1; **14**, 84928-47-2; diphenylphosphine, 829-85-6; 2-cyclohexylideneethyl chloride, 61638-81-1; (2-cyclohexylideneethyl)diphenylphosphine oxide, 13303-59-8; ethoxyacetylene, 927-80-0; methyltriphenylphosphonium bromide, 1779-49-3.

A New 2-Azatricyclo[4.4.0.0^{2,8}]decenone Synthesis and Ketene Formation by Retro-Diels–Alder Reaction

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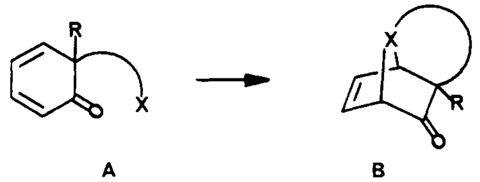
Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. *Received August 5, 1982*

Abstract: 6-(3-Azidopropyl)-2,4-cyclohexadien-1-ones **2c** and **2d** and 6-(o-azidobenzyl)-2,4-cyclohexadien-1-ones **7a** and **7b** are prepared by C-alkylation of 2,4,6-trialkyl-substituted phenols. These azides provide triazolines **3a**, **3b**, **8a**, and **8b** by thermal intramolecular azide–olefin cycloaddition. Photochemical conversion of triazolines to 2-azatricyclo[4.4.0.0^{2,8}]dec-9-en-7-ones **4a**, **4b**, and **10a** with 366-nm light accomplished the synthetic equivalence of an intramolecular cycloaddition between a diene and a nitrene; e.g., **2** → **3** → **4**. Thermolysis of **7a** and **7b** provides triazolines **8**, aziridines **9**, and azatricyclodecenones **10**. Pyrex-filtered or 366-nm irradiation of **8a**, **9a**, and **10a** gives dienone **11** as the major reaction product. Pyrex-filtered irradiation of azatricyclodecenones in methanol results in photoinitiated retro-Diels–Alder reaction to give pyrrole ketenes (e.g., **5a** and **5b**), which undergo reaction with methanol to give pyrrole methyl esters **6a**, **6b**, **12a**, and **12b**. The preparation and photochemistry of triazolines **17a** and **17b** also are described.

There has been remarkable interest in the development of intramolecular cycloaddition processes during the past decade. Diels–Alder reactions,[1] dipolar cycloadditions,[2] and photochemical cyclobutane formation,[3] when performed intramolecularly, often display exceptional regio- and stereochemical control. The related conversion A → B (X = N) has not been exploited because nitrenes generally react with conjugated dienes to give vinylaziridines.[4]

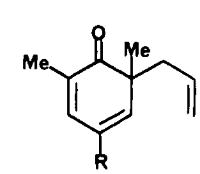


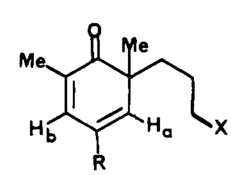
A B

We wish to report that triazolines formed by intramolecular dipolar cycloaddition of 6-(3-azidopropyl)-2,4-cyclohexadien-1-ones undergo eliminative rearrangement to 2-azatricyclo[4.4.0.0^{2,8}]dec-9-en-7-ones; e.g., **2** → **3** → **4**. This two-step sequence provides a method for accomplishing the synthetic equivalence of an intramolecular cycloaddition between a diene and a nitrene. We also describe photochemical conversions of 2-azatricyclodec-9-en-7-ones **4** and **10** to pyrrolecarboxylic acid derivatives **6** and **12**, presumably via photoinitiated retro-Diels–Alder reaction of **4** and **10** to give intermediate pyrrole ketenes; e.g., **5**.

Results and Discussion

(Azidopropyl)cyclohexadienone **2c** is prepared from 2,4,6-trimethylphenol by (1) C-alkylation with allyl bromide as described by Miller[5] to give **1a**, (2) hydroboration of **1a** with disiamylborane





1a, R = Me
b, R = t-Bu

2a, R = Me; X = OH
b, R = Me; X = OMs
c, R = Me; X = N_3
d, R = t-Bu; X = N_3

in THF followed by oxidative workup with H_2O_2/NaOH to give **2a** (68% isolated yield), (3) treatment of **2a** with methanesulfonyl chloride in triethylamine/CH_2Cl_2 to give **2b** (99%), and (4) reaction of **2b** with sodium azide in DMF to give **2c** in 96% yield. In similar fashion 4-$tert$-butyl-2,6-dimethylphenol[6] is converted

(1) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63.
(2) Padwa, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 123.
(3) Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135.
(4) Patai, S. "The Chemistry of the Azido Group"; Interscience: New York, 1971.
(5) (a) Miller, B. *J. Am. Chem. Soc.* **1965**, *87*, 5115. (b) Miller, B. *J. Org. Chem.* **1970**, *35*, 4262.
(6) Curtin, D. Y.; Dybvig, D. H. *J. Am. Chem. Soc.* **1962**, *84*, 225.
(7) For the preparation of an analogue of **4** by an interesting intramolecular Diels–Alder addition of N-4-pentenylisoindole, see: Ciganek, E. *J. Org. Chem.* **1980**, *45*, 1512.
(8) Ripoll, J. L.; Rouessac, A.; Rouessac, R. *Tetrahedron* **1978**, *34*, 19.
(9) For recent characterization of radiation-sensitive 2-diazoketones, see: Hacker, N. P.; Turro, J. J. *Tetrahedron Lett.* **1982**, *23*, 1771; Pacansky, J.; Chang, J. S.; Brown, D. W.; Schwarz, W. *J. Org. Chem.* **1982**, *47*, 2233.

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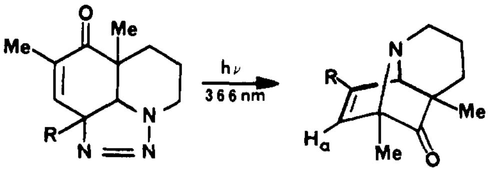
to **1b** and thence to **2d** in 39% overall isolated yield.

(Azidopropyl)cyclohexadienone **2c** undergoes intramolecular azide–olefin cycloaddition in refluxing benzene solution to give triazoline **3a** in 43% isolated yield. A second compound isolated

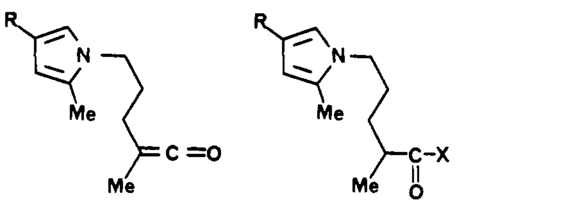


3a, R = Me   4a, R = Me
b, R = *t*-Bu   b, R = *t*-Bu

from thermolysis of **2c** (36% yield) gives elemental analysis compatible with the formula $C_{12}H_{17}N_3O$, indicating that it is isomeric with **3a**. Current spectroscopic information does not provide a unique structural assignment for this substance. Triazoline **3b** is formed from **2d** in refluxing toluene solution in 91% isolated yield.

The key eliminative rearrangement of **3a** to azatricyclodecenone **4a** is accomplished in 79% yield by irradiation with 366-nm light (0.01 M in methanol; 30-min irradiation). Similarly, **3b** gives crystalline **4b** in 97% yield.[7]

It is essential that light of wavelength ~366 nm be used for the conversion of **3** to **4**. Pyrex-filtered irradiation of **3a** or **3b** in methanol solution gives pyrrole methyl ester **6a** (85% isolated yield) or **6b** (90%). Irradiation of **4a** or **4b** also gives **6a** or **6b**



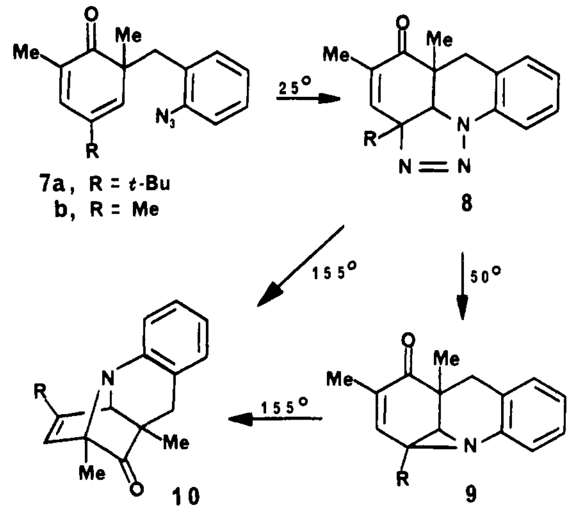
5a, R = Me   6a, R=Me ; X = OMe
b, R = *t*-Bu   b, R=*t*-Bu ; X = OMe
c, R=*t*-Bu ; X = OH
d, R=*t*-Bu ; X = N(CH₂)₄

in comparable yield. This wavelength effect is due to the fact that with 366-nm light, the α,β-enone chromophore in **3** is absorbent; however, at 366 nm, the β,γ-enone chromophore in **4** does not absorb a significant amount of light. Thus, the photochemical production of pyrrole methyl esters on Pyrex-filtered irradiation of triazolines **3** is most probably a two-photon process.

With regard to a mechanism for conversions of **4** to **6**, we presume that photoinitiated retro-Diels–Alder reactions of **4a** and **4b**[8] give intermediate pyrrole ketenes **5a** and **5b**; these react with methanol to afford the isolated pyrrole methyl esters **6a** and **6b**. In support of the intermediacy of ketene **5b**, we find that carboxylic acid **6c** (92%) and amide **6d** (98%) are formed on Pyrex-filtered irradiation of **3b** in THF–H_2O and THF–pyrrolidine solutions, respectively.

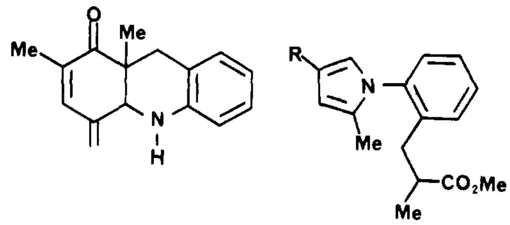
Photochemical ketene generation has been used in photoimaging processes that require positive photoresists in polymer films.[9] With such applications in mind, we have developed a one-step synthesis of 6-(*o*-azidobenzyl)-2,4-cyclohexadien-1-ones **7a** (92% yield) and **7b** (87%) by phenolic alkylation (NaOMe, benzene, 0–5 °C) with *o*-azidobenzyl bromide.[10]

A careful study of the thermal chemistry associated with **7a** and **7b** has resulted in selective access to triazolines **8**, aziridines **9**, and azatricyclodecenones **10**. In ether solution at 25 °C, **7a** undergoes cyclization to triazoline **8a**; at 100 °C, triazoline **8a** is converted to aziridine **9a**. Both **8a** and **9a** undergo thermal rearrangement to **10a** in Decalin solution at 150 °C. Analogous reactions with **7b** provide triazoline **8b**, aziridine **9b**, and azatricyclodecenone **10b**.



7a, R = *t*-Bu
b, R = Me
8
9
10

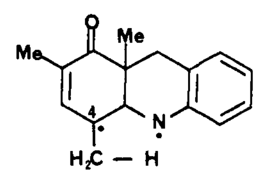
Photoconversion of triazoline **8a** to **10a** (>95%) is accomplished with 366-nm light. Interestingly, aziridine **9a** also gives **10a** in comparable yield. With Pyrex-filtered light **8a**, **9a**, and **10a** (methanol solution) all are converted to pyrrole methyl ester **12a**.



11   12a, R = *t*-Bu
b, R = Me

However, 366-nm or Pyrex-filtered irradiation of **8b** and **9b** gives dienone **11** as the major reaction product (75%). As expected, pyrrole methyl ester **12b** is formed on Pyrex-filtered irradiation of **10b** in methanol.

These experiments show that there is a distinct difference between the photochemical reactivities of **8a** and **8b**. Apparently diradical **13**, produced by photoelimination of molecular nitrogen from **8b**, undergoes H-atom transfer from the C(4) methyl substituent to give **11**, but the thermally produced diradical **13** un-



13

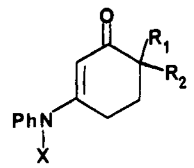
dergoes radical recombination to give **10b**. These reactivities may reflect a difference in multiplicity between the photochemically and thermally generated diradicals. Additional studies are required in order to explore this interesting possibility.

We also have studied the photochemistry of triazolines **17**.[11] These are prepared by a 1,3-cyclohexanedione-based route to 2,4-cyclohexadien-1-ones. Enaminone **14a** is sequentially alkylated

(10) Chou, S. P. Ph.D. Thesis, University of Michigan, 1979. Barton, D. H. R.; Sammes, P. G.; Weingarten, G. G. *J. Chem. Soc. C* **1971**, 721.

(11) For a preliminary report of the photochemistry of **17a**, see: Schultz, A. G.; Sha, C.-K. *J. Org. Chem.* **1980**, *45*, 2040.

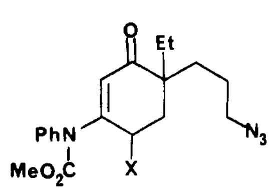
(12) For reactions of enaminones, see: Vinick, F. J.; Gschwend, H. W. *Tetrahedron Lett.* **1978**, 315 and references cited therein.



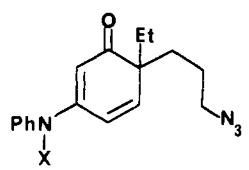
14a, $R_1 = R_2 = H$; $X = CH_2Ph$
b, $R_1 = H$; $R_2 = Et$; $X = CH_2Ph$
c, $R_1 = CH_2CH_2CH_2Cl$; $R_2 = Et$; $X = CH_2Ph$
d, $R_1 = CH_2CH_2CH_2Cl$; $R_2 = Et$; $X = H$
e, $R_1 = CH_2CH_2CH_2Cl$; $R_2 = Et$; $X = CO_2Me$

with ethyl iodide to give **14b** and 1-bromo-3-chloropropane to give **14c**.[12] Debenzylation of **14c** gives **14d**, and treatment of **14d** with KH in THF followed by methyl chloroformate results in a mixture of urethane **14e** and O-acylated product. On the other hand, treatment of the lithium salt of **14d** (generated by reaction of **14d** with *n*-butyllithium) with methyl chloroformate gives urethane **14e** in quantitative yield.

Urethane **14e** is converted to **15a** on reaction with sodium azide in DMF. Bromination of **15a** with *N*-bromosuccinimide and



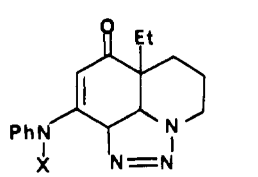
15a, X = H
b, X = Br



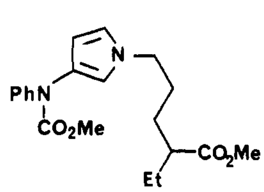
16a, $X = CO_2Me$
b, X = H

azobis(isobutyronitrile) in CCl_4 gives **15b**, which undergoes elimination of HBr on treatment with tetraethylammonium acetate, thus producing azido dienone **16a** in 80% overall yield. Enaminone **16b** is obtained by reaction of urethane **16a** with sodium methoxide in methanol.

Triazolines **17a** and **17b** are prepared from their respective (azidopropyl)cyclohexadienones. Brief Pyrex-filtered irradiation



17a, $X = CO_2Me$
b, X = H



18

of **17a** in methanol solution gives pyrrole methyl ester **18** in essentially quantitative yield (75% isolated yield). Irradiation of **17a** in benzene solution gives a cyclobutane-1,3-dione dimer of the photogenerated ketene as the major reaction product. The stereochemistry of this dimer has not been determined; the assignment of structure is based primarily on chemical ionization mass spectral analysis (*m/e* 653), ^1H and ^{13}C NMR data, and the presence of infrared absorption at 1810 cm^{-1}. Furthermore, the dimeric substance is converted to **18** on treatment with sodium methoxide in methanol at room temperature.

Thus far, we have not been able to isolate an azatricyclodecenone corresponding to **4** from photolysis of triazoline **17a**. A detailed study of the photochemical, thermal, and transition-metal-catalyzed reactions of triazolines is in progress and, at this stage, we have discovered a subtle structural requirement for photoreactivity. Irradiation of triazoline **17b** in either benzene or methanol (under conditions resulting in commplete consumption of **17a**) gives mostly recovered starting material. Comparison of UV spectra of **17a** and **17b** reveals a shift of absorption of the enone chromophore in **17b** toward longer wavelength. This may mean that the lowest excited state in **17b** has energy localized in the enone chromophore and that this electronic energy is not efficiently transferred to the triazoline group. These observations suggest that it may be possible to perform selective photochemistry with multifunctional triazolines.

Finally, while the stereochemistry in structures **3**, **8**, **9**, **11**, **13**, and **17** has not been indicated, we presume that all these compounds possess cis ring fusions. The *cis*-azaoctalone ring fusions are tentatively assigned on the basis of the conversions to azatricyclodecenones. The remaining stereochemistry follows from the established cis mode of addition for azide–olefin cycloadditions.[13]

Summary

We have described an efficient synthesis of 2-azatricyclo-[4.4.0.0^{2,8}]dec-9-en-7-ones from 2,4,6-trialkyl-substituted phenols. The new photochemical retro-Diels–Alder generation of ketenes may be of value in relation to photoresist chemistry. At present we are exploring the application of chemistry developed in this study to the synthesis of natural products. We also are involved in development of an analogous synthetic equivalence of an intramolecular cycloaddition between a diene and a carbene; e.g., A → B (X = CR).

Experimental Section

Instrumentation. ^1H NMR spectra were obtained on Varian T-60 (60 MHz), Varian XL-200 (200 MHz), or Hitachi–Perkin-Elmer R-600 (60 MHz) NMR spectrometers with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on the Varian XL-200 spectrometer. Infrared spectra were recorded on either a Perkin-Elmer 137b or 298 spectrometer. Ultraviolet spectra were obtained on a Perkin-Elmer 552 spectrophotometer. Melting points were measured on a calibrated Thomas-Hoover capillary melting point apparatus and are reported uncorrected. Mass spectra were obtained on a Finnigan OWA-1020, 3300 gas chromatograph–mass spectrometer (GC/MS) or a Hitachi–Perkin-Elmer RMU-6E mass spectrometer. Mass spectrum refers to electron impact mass spectrum unless otherwise specified.

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 argon 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.

Preparative silica gel thin-layer plates were made of E. Merck AG Darmstadt silica gel PF-254 or GF-254. Preparative alumina thin-layer chromatography (TLC) was performed with alumina GF-2000 from Anal Tech. Silica gel column chromatography was performed with Woelm silica gel (Activity III) from ICN and flash chromatography was performed with silica gel 60 from EM Reagents. Preparative high-pressure chromatography (HPLC) was performed on a Waters Associates Preparative LC 500 Unit.

Analytical vapor-phase chromatography (VPC) was performed on a Hewlett-Packard HP 5710A gas chromatograph equipped with a flame ionization detector (300 °C) and nitrogen carrier gas. The column used for all analyses consisted of a 20 in. × $^1/_8$ in. stainless-steel tube filled with 10% UC W-982 on Chromosorb W, 80–100 mesh size. Peak areas were measurd with a HP 3380A integrator. Microanalyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI, or Galbraith Laboratories, Knoxville, TN.

Solvents. Tetrahydrofuran (THF) was dried by distillation in the presence of potassium metal under a nitrogen atmosphere with benzophenone ketyl as indicator.

Hexamethylphosphoramide (HMPA) and dimethylformamide (DMF) were distilled at reduced pressure from calcium hydride and stored over 4-Å molecular sieves under a nitrogen atmosphere. Triethylamine and

(13) Scheiner, P.; Schomaker, J. H.; Deming, S.; Libbey, W. J.; Nowack, G. P. *J. Am. Chem. Soc.* **1965**, *87*, 306. Huisgen, R.; Mobius, L.; Mueller, G.; Stangl, H.; Szeimies, G.; Vernon, J. M. *Chem. Ber.* **1965**, *98*, 3992. Huisgen, R.; Szeimies, G. *Ibid.* **1965**, *98* 1153. Scheiner, P. *J. Am. Chem. Soc.* **1966**, *88*, 4759.

(14) Brown, H. C. "Organic Synthesis via Boranes"; Wiley: New York, 1975.

diisopropylamine were distilled from calcium hydride and stored over 4-Å molecular sieves. Methylene chloride was distilled from phosphorus pentoxide and stored over 4-Å molecular sieves. Mallinckrodt anhydrous ethyl ether was used without further purification, and dry methanol was obtained via distillation over magnesium turnings. Aldrich spectrophotometric grade methanol was used as a solvent for photoreactions.

Solvents were removed at reduced pressure with a Büchi Rotovapor-R rotary evaporator. The last traces of solvent were removed by evacuation at room temperature using a Welch Duo-Seal floor pump (~0.05 mmHg).

6-(3-Hydroxypropyl)-2,4,6-trimethyl-2,4-cyclohexadien-1-one (2a). Disiamylborane[14] (41.2 mL, 0.5 M in THF) was added dropwise over 30 min to a solution of 6-allyl-2,4,6-trimethyl-2,4-cyclohexadien-1-one[5a] (2.33 g, 0.013 mol) in dry THF (18 mL) at 0 °C. After 3.5 h, excess borane was destroyed with water at 0 °C. On removing the cooling bath a solution of NaOH (7.7 mL, 3 M) was added, after which hydrogen peroxide (7.7 mL, 30%) was added dropwise at a rate that maintained the reaction temperature below 50 °C. The reaction mixture was stirred for 2 h at room temperature. Excess sodium chloride was added and the mixture was extracted with ether.

The organic extracts were combined and dried ($MgSO_4$), and solvent was evaporated under reduced pressure to give crude **2a**. Preparative HPLC (hexane–ethyl acetate 1.8:1) afforded **2a** (1.69 g, 67%). ^1H NMR ($CDCl_3$) δ 1.12 (s, 3 H), 1.2–1.8 (m, 4 H), 1.86 (br s overlapping d at 1.92, 6 H, J = 1.5 Hz), 3.46 (t, 2 H, J = 6 Hz), 5.85 (br s, 1 H, H_a), 6.73 (br s, 1 H, H_b); IR (film) 3300, 1640, 1580 cm^{-1}; mass spectrum, m/e 194 (M^+).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.18; H, 9.44.

Mesylate 2b. To a solution of alcohol **2a** (1.24 g, 6.39 mmol) in dry methylene chloride (30 mL) was added triethylamine (1.4 g, 14 mmol) and methanesulfonyl chloride (1.46 g, 13 mmol). The resulting mixture was stirred overnight at room temperature. The reaction mixture was washed with water and the combined aqueous extracts were extracted with methylene chloride. The combined organic layers were washed with brine and dried (Na_2SO_4), and solvent was evaporated under reduced pressure to afford mesylate **2b** (1.74 g, 99%), which was used immediately without further purification. ^1H NMR ($CDCl_3$) δ 1.14 (s, 3 H), 1.3–1.8 (m, 4 H), 1.87 (br s overlapping d at 1.93, 6 H, J = 1.5 Hz), 2.98 (s, 3 H), 4.10 (t, 2 H, J = 6 Hz), 5.83 (br s, 1 H, H_a), 6.74 (br s, 1 H, H_b); IR (film) 1650, 1590 cm^{-1}.

6-(3-Azidopropyl)-2,4,6-trimethyl-2,4-cyclohexadien-1-one (2c). A mixture of mesylate **2b** (0.460 g, 1.69 mmol) and sodium azide (0.238 g, 3.66 mmol) in dry DMF (10 mL) was stirred at room temperature for 24 h. The solvent was removed on a rotary evaporator equipped with a mechanical vacuum pump. The residue was partitioned between ether/methylene chloride (3:1) and water. The water layer was extracted with ether–methylene chloride. The combined organic extracts were washed successively with 1 N sodium bicarbonate, water, and brine and then dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded crude **2c** (0.36 g, 97%). Chromatography was carried out by HPLC (hexane–ethyl acetate 25:1) to give azide **2c**; oil (0.34 g, 90%): ^1H NMR ($CDCl_3$) δ 1.13 (s, 3 H), 1.27–1.54 (m, 4 H), 1.88 (br s overlapping d at 1.92, 6 H, J = 1.6 Hz), 3.14 (t, 2 H, J = 6 Hz), 5.82 (br s, 1 H, H_a), 6.72 (br s, 1 H, H_b); IR (film) 2090, 1650, 1590 cm^{-1}; mass spectrum, m/e 190 (M^+ – 29), 176 (M^+ – 43); UV (MeOH) λ_{max} 318 nm (ε 3950).

Anal. Calcd for $C_{12}H_{17}N_3O$: C, 65.72; H, 7.82. Found: C, 65.94; H, 7.93.

4-*tert*-Butyl-2,6-dimethyl-6-(3-azidopropyl)-2,4-cyclohexadien-1-one (2d). A solution of 6-allyl-4-*tert*-butyl-2,6-dimethyl-2,4-cyclohexadien-1-one[5b] (2.21 g, 0.10 mol) in dry THF (10 mL) was cooled to 0 °C. Disiamylborane (34 mL, 0.5 M) was added dropwise over a 20-min period and the resulting solution was stirred for 2.5 h at 0 °C. Excess borane was destroyed with water at 0 °C, after which the cooling bath was removed. Oxidation with sodium hydroxide solution (6.33 mL, 3 M) and hydrogen peroxide (6.36 mL, 30%) was carried out as described for **2a**. Extraction with ether, drying ($MgSO_4$), and evaporation under reduced pressure gave crude 4-*tert*-butyl-2,6-dimethyl-6-(3-hydroxypropyl)-2,4-cyclohexadien-1-one. Chromatography by HPLC (hexane–ethyl acetate 1.8:1) afforded alcohol (1.62 g, 68%). ^1H NMR ($CDCl_3$) δ 1.5 (overlapping s, 12 H), 1.25–1.6 (m, 4 H), 1.89 (br s, 3 H), 3.46 (t, 2 H, J = 6 Hz), 5.87 (br s, 1 H, H_a), 7.01 (br s, 1 H, H_b); IR (film) 3340, 1640, 1580 cm^{-1}; mass spectrum, m/e 236 (M^+).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.04; H, 10.32.

A solution of the alcohol (1.27 g, 5.38 mmol) in dry methylene chloride (25 mL) was cooled to 0 °C and treated sequentially with triethylamine (1.20 g, 11.9 mmol) and methanesulfonyl chloride (1.24 g, 10.8 mmol). The resulting mixture was stirred overnight at room temperature. Reaction workup as described for **2b** afforded crude mesylate (1.68 g, 99%), which was used immediately without purification in the next step. ^1H NMR ($CDCl_3$) δ 1.15 (s, 12 H), 1.3–1.8 (m, 4 H), 1.9 (br s, 3 H), 2.98 (s, 3 H), 4.09 (t, 2 H, J = 6 Hz), 5.85 (br s, 1 H, H_a), 7.01 (br s, 1 H, H_b); IR (film) 1650, 1590 cm^{-1}.

A solution of the mesylate (0.163 g, 0.519 mmol) in dry DMF (5 mL) was treated with sodium azide (0.04 g, 0.6 mmol). The resulting suspension was stirred at room temperature for 24 h. Reaction workup as described for **2c** provided crude **2d** (0.126 g, 93%) as a yellow oil. Further purification was done by HPLC (hexane–ethyl acetate; 25:1) to give pure **2d** (0.115 g, 85%) as an oil, which crystallized on cooling: mp 44–45.5 °C; ^1H NMR ($CDCl_3$) δ 1.15 (s, 12 H), 1.25–1.63 (m, 4 H), 1.90 (br s, 3 H), 3.13 (t, 2 H, J = 6 Hz), 5.85 (br s, 1 H, H_a), 7.01 (br s, 1 H, H_b); IR (film) 2090, 1650, 1590 cm^{-1}; mass spectrum, m/e 232 (M^+ 29), 218 (M^+ – 43), 190 (M^+ – 71); UV (MeOH) λ_{max} 315 nm (ε 4200).

Anal. Calcd for $C_{15}H_{23}N_3O$: C, 68.93; H, 8.87. Found: C, 68.82; H, 8.84.

5,6,6a,7,9a,9b-Hexahydro-7-oxo-6a,8,9a-trimethyl-4*H*-1,2,3-triazolo[4,5,1-*ij*]quinoline (3a). A solution of **2c** (0.441 g, 2.01 mmol) in dry benzene (66 mL) was heated at reflux temperature for 21 h, after which TLC analysis revealed the presence of two reaction products. The solvent was removed under reduced pressure and the residue was chromatographed by HPLC (hexane–ethyl acetate 6:1). Triazoline **3a** (0.191 g, 43%) was obtained as a white crystalline solid, which was recrystallized from hexane: mp 89–90 °C; ^1H NMR ($CDCl_3$) δ 1.07 (m with overlapping s at 1.16, 4 H), 1.57 (m, 2 H), 1.69 (s, 3 H), 1.78 (d, 3 H, J = 1.6 Hz), 2.54 (m, 1 H), 2.66 (s, 1 H), 3.02 (m, 1 H), 4.24 (m, 1 H), 6.11 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.59, 21.90, 24.03, 24.38, 33.51, 43.07, 47.31, 69.21, 75.39, 134.39, 134.95, 200.23; IR (CH_2Cl_2) 1675 cm^{-1}; mass spectrum, m/e 191 (M^+ – 28); UV (MeOH) λ_{max} 226 nm (ε 14 000), 258 (5500) with tailing to ~380 nm.

Anal. Calcd for $C_{12}H_{17}N_3O$: C, 65.72; H, 7.82; N, 19.16. Found: C, 65.64; H, 7.89; N, 19.05.

In addition to **3a** another product isomeric with **3a** was isolated (0.16 g, 36%) as a white crystalline solid, which was recrystallized from hexane: mp 79–80 °C; ^1H NMR ($CDCl_3$) δ 1.1 (s, 3 H), 1.2 (s overlapping m at 1.32, 4 H), 1.58 (m, 2 H), 1.78 (m, 1 H), 1.94 (s, 3 H), 2.9 (m, 1 H), 4.4 (m, 1 H), 4.8 (s, 1 H), 5.1 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.45, 19.83, 26.57, 27.98, 38.18, 47.88, 48.16, 63.35, 91.79, 127.97, 129.73, 207.85; IR ($CHCl_3$) 1710 cm^{-1}; mass spectrum, m/e 191 (M^+ – 28); UV (MeOH) λ_{max} 271 nm (ε 4500) with tailing to ~340 nm.

Anal. Calcd for $C_{12}H_{17}N_3O$: C, 65.72; H, 7.82; N, 19.16. Found: C, 65.64; H, 7.94; N, 19.00.

9a-*tert*-Butyl-6a,8-dimethyl-5,6,6a,7,9a,9b-hexahydro-7-oxo-4*H*-1,2,3-triazolo[4,5,1-*ij*]quinoline (3b). A solution of azide **2d** (0.739 g, 2.83 mmol) in dry toluene (100 mL) was heated to reflux temperature for 5.5 h. The solvent was removed under reduced pressure and the residue was chromatographed by HPLC (hexane–ethyl acetate; 8:1) to provide pure triazoline **3b** (0.673 g, 91%) as an oil, which crystallized on cooling. Recrystallization form hexane gave white needles: mp 104–106 °C; ^1H NMR ($CDCl_3$) δ 1.08 (s, 9 H), 1.13 (s, 3 H), 1.21 (m, 1 H), 1.57 (m, 1 H), 1.8 (s, 3 H), 2.57 (m, 1 H), 3.13 (m with overlapping s at 3.18, 2 H), 4.31 (m, 1 H), 6.58 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.4, 21.74, 26.56, 27.87, 33.74, 35.91, 43.17, 46.82, 62.29, 86.33, 134.14, 136.26, 201.03; IR ($CDCl_3$) 1675 cm^{-1}; mass spectrum, m/e 233 (M^+ – 28); UV (MeOH) λ_{max} 228 nm (ε 13 300) with tailing to ~380 nm.

Anal. Calcd for $C_{15}H_{23}N_3O$: C, 68.93; H, 8.87; N, 16.08. Found: C, 69.08; H, 9.01; N, 15.99.

2-Aza-6,8,10-trimethyltricyclo[4.4.0.0^{2,8}]dec-9-en-7-one (4a). A solution of triazoline **3a** (30.6 mg, 0.139 mmol) in methanol (15.3 mL) was irradiated with the 366-nm light source for 30 min. The solvent was removed in vacuo and the residue was partitioned between methylene chloride and water. The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to afford crude **4a** (25.4 mg, 96%). Column chromatography on silica gel (hexane–ethyl acetate 3:1) gave **4a** (21 mg, 79%) as an oil: ^1H NMR ($CDCl_3$) δ 1.03 (s, 3 H), 1.17–1.8 (m with overlapping s at 1.31, 7 H), 1.92 (d, 3 H, J = 1.6 Hz), 3.05 (m, 2 H), 3.39 (s, 1 H), 5.60 (br s, 1 H, H_a); IR (film) 1730 cm^{-1}; mass spectrum, m/e 163 (M^+ – 28), 148 (M^+ – 43); UV (MeOH) λ_{max} 215 nm (ε 4600), 319 (230) with tailing to 360 nm.

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96. Found: C, 74.33; H, 9.12.

2-Aza-10-*tert*-butyl-6,8-dimethyltricyclo[4.4.0.0^{2,8}]dec-9-en-7-one (4b). A solution of triazoline **3b** (32.7 mg, 0.125 mmol) in methanol (16.4 mL) was irradiated with the 366-nm light source for 30 min. Workup as described for **4a** afforded crude **4b** (28.0 mg, 97%). Column chromatography on silica gel (hexane–ethyl acetate 3:1) afforded **4b** (24.9 mg, 86%) as an oil, which crystallized on cooling: mp 45–46 °C; ^1H NMR ($CDCl_3$) δ 1.04 (s overlapping s at 1.10, 12 H), 1.32 (s, overlapping m at 1.53, 7 H), 3.01 (m, 2 H), 3.63 (d, 1 H, $J = 2$ Hz), 5.59 (d, 1 H, $J = 1.6$ Hz, H_a); IR ($CDCl_3$) 1725 cm^{-1}; mass spectrum, m/e 205 ($M^+ - 28$), 190 ($M^+ - 43$); UV (MeOH) λ_{max} 217 nm (ϵ 6000), 317 (300) with tailing to ~340 nm.

Anal. Calcd for $C_{15}H_{23}NO$: C, 77.20; H, 9.93. Found: C, 77.21; H, 10.02.

Pyrrole Carboxylic Ester 6a. A solution of triazoline **3a** (5.3 mg, 0.024 mmol) in methanol (3 mL) was irradiated through Pyrex glass for 30 min. The solvent was removed at reduced pressure and the residue partitioned between ether and water. The organic extract was washed with brine and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure afforded **6a** (4.6 mg, 85%): ^{1}H NMR ($CDCl_3$) δ 1.16 (d, 3 H, $J = 8$ Hz), 1.34–1.76 (m, 4 H), 2.06 (s, 3 H), 2.17 (s, 3 H), 2.46 (m, 1 H), 3.68 (s overlapping m, 5 H), 5.7 (br s, 1 H), 6.32 (br s, 1 H); IR (film) 1730 cm^{-1}; mass spectrum, m/e 223 (M^+).

Pyrrole Carboxylic Ester 6b. A solution of **3b** (8.4 mg, 0.032 mmol) in methanol (3 mL) was irradiated throgh Pyrex glass for 30 min. Workup as described for **6a** afforded **6b** (6.9 mg, 81%). The product, which appeared to be of good purity by NMR analysis, could be further purified by Kugelrohr distillation (bp 115–120 °C, 0.75 mmHg). ^{1}H NMR ($CDCl_3$) δ 1.16 (d overlapping s at 1.2, 12 H, $J = 8$ Hz), 1.34–1.8 (m, 4 H), 2.17 (s, 3 H), 2.46 (m, 1 H), 3.67 (s overlapping m, 5 H), 5.79 (br s, 1 H), 6.32 (br s, 1 H); IR (film) 1730 cm^{-1}; mass spectrum, m/e 265 (M^+).

Anal. Calcd for $C_{16}H_{27}NO_2$: C, 72.41; H, 10.26. Found: C, 72.17; H, 10.12.

Pyrrole Carboxylic Acid 6c. A solution of triazoline **3b** (6.9 mg, 0.026 mmol) in THF–water (2:1, 3 mL) was irradiated through Pyrex glass for 30 min. The reaction mixture was extracted with ether and the combined organic extracts were dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded **6c** (6 mg, 92%); ^{1}H NMR ($CDCl_3$) δ 1.2 (s overlapping d, 12 H), 1.4–1.82 (m, 2 H), 2.18 (s, 3 H), 2.46 (m, 1 H), 3.72 (m, 2 H), 5.82 (br s, 1 H), 6.43 (br s, 1 H); IR (film) 3700–2300, 1710 cm^{-1}. On treatment with diazomethane in ether, **6c** was converted to **6b**.

Pyrrole Amide 6d. A solution of triazoline **3b** (4.7 mg, 0.018 mmol) and pyrrolidine (18 μL, 0.216 mmol) in dry THF (3 mL) was irradiated through Pyrex glass for 30 min. Evaporation of the solvent yielded **6d** (5.4 mg): ^{1}H NMR ($CDCl_3$) δ 1.1 (d, 3 H, $J = 8$ Hz), 1.32–2.0 (m, 4 H), 2.16 (s, 3 H), 2.48 (m, 1 H), 3.44 (m, 4 H), 3.69 (m, 2 H), 5.8 (br s, 1 H), 6.34 (br s, 1 H); IR (film) 1640 cm^{-1}.

Anal. Calcd for $C_{19}H_{32}N_2O$: C, 74.95; H, 10.59. Found: C, 72.42; H, 10.30.

Photolysis of 2-Azatricyclo[4.4.0.0^{2,8}]decenone 4a. A solution of **4a** (4.0 mg, 0.021 mmol) in methanol (3 mL) was irradiated through Pyrex glass for 30 min. The solvent was removed under reduced pressure and the residue was dissolved in methylene chloride. The organic extract was dried ($MgSO_4$) and concentrated under vacuum to give **6a** (4.6 mg).

Photolysis of 4b. A solution of **4b** (3.6 mg, 0.015 mmol) in methanol (3.5 mL) was irradiated through Pyrex glass for 30 min. The solvent was removed under reduced pressure and the residue was dissolved in methylene chloride, dried ($MgSO_4$), and concentrated to afford **6b** (4 mg).

6-(*o*-Azidobenzyl)-2,6-dimethyl-4-*tert*-butyl-2,4-cyclohexadien-1-one (7a). To 2,6-dimethyl-4-*tert*-butylphenol[6] (3.0 g, 17 mmol) dissolved in dry benzene (20 mL) was added sodum methoxide (0.95 g, 18 mmol). After the resulting green suspension was mechanically stirred for 18 h at room temperature, 6.5 mL of solvent was removed by distillation at atmospheric pressure. To the suspension was added *o*-azidobenzyl bromide (17 g, 5.5 mmol) at 0 °C, and the resulting mixture was stirred for 4 days at 0–5 °C. A precipitate was removed by filtration, and the filtrate was washed with Claisen alkali (3 × 30 mL), water (5 × 30 mL), and brine (1 × 30 mL), dried ($MgSO_4$), and concentrated to give a mixture of yellow oil (1.62 g, 87%) and white crystals (0.15 g, 8%). ^{1}H NMR of the oil showed the presence of **7b** and a small amount (6%) of *o*-azidobenzyl 2,4,6-trimethylphenyl ether. **7a**: ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9 H), 1.24 (s, 3 H), 1.83 (br s, 3 H), 2.97 (m, 2 H), 6.02 (m, 1 H), 6.76 (m, 1 H), 6.90–7.45 (m, 4 H); IR (film) 2125, 1635, 1290, 754 cm^{-1}. The crude oil kept at room temperature gave additional crystalline material, which was characterized (vide infra) as triazoline **8a**.

6-(*o*-Azidobenzyl)-2,4,6-trimethyl-2,4-cyclohexadien-1-one (7b). A stirred solution of 2,4,6-trimethylphenol (3.0 g, 22 mmol) in benzene (15 mL) was treated with sodium methoxide (1.10 g, 20 mmol) and then with *o*-azidobenzyl bromide (1.6 g, 7.1 mmol) as described for preparation of **7a**. Crystalline material (~40 mg) was separated by filtration (a small amount of ethyl ether was used to wash the crystals) and the filtrate was concentrated to afford a yellow oil (1.57 g, 92%). ^{1}H NMR of the oil showed the presence of azide **7b** and of *o*-azidobenzyl 2,6-dimethyl-4-*tert*-butylphenyl ether (18%). **7b**: ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 3 H), 1.81 (s, 3 H), 1.82 (s, 3 H), 2.95 (d, 2 H, $J = 1$ Hz), 5.98 (m, 1 H), 6.53 (m, 1 H), 6.95–7.32 (m, 4 H); IR (film) 2110, 1642, 1290, 754 cm^{-1}. The crude oil kept at room temperature gave additional crystalline material, which was characterized (vide infra) as triazoline **8b**.

9a-*tert*-Butyl-6a,8-dimethyl-5,6,6a,7,9a,9b-hexahydro-7-oxo-4*H*-1,2,3-triazolo[4,5,1-*ij*]benz[*b*]quinoline (8a). A solution of azide **7a** (1.57 g, 5.1 mmol) in ethyl ether (10 mL) was kept at room temperature for 17 days to give triazoline **8a** (0.66 g). Additional triazoline **8a** (98 mg) was isolated after 24 days: mp 132–134 °C (recrystallized from THF–water); ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9 H), 1.32 (s, 3 H), 1.80 (d, 3 H, $J = 1.3$ Hz), 2.60 (d, 1 H, $J = 17$ Hz), 3.63 (d, 1 H, $J = 17$ Hz), 3.75 (d, 1 H, $J = 1.3$ Hz), 6.65 (br s, 1 H), 7.00 (t, 1 H, $J = 8$ Hz), 7.14–7.32 (m, 2 H), 7.68 (d, 1 H, $J = 8$ Hz); IR (Nujol) 1667, 1131 cm^{-1}; UV (MeOH) λ_{max} 207 nm (ϵ 21 200), 234 (15 700), 270 (5780), 303 (4130), 335 (4360).

Anal. Calcd for $C_{19}H_{23}ON_3$: C, 73.75; H, 7.49. Found: C, 73.84; H, 7.50.

5,6,6a,7,9a,9b-Hexahydro-7-oxo-4,8,9a-trimethyl-4*H*-1,2,3-triazolo-[4,5,1-*ij*]benz[*b*]quinoline (8b). A solution of azide **7b** (crude, 1.62 g, 6.1 mmol) in ether (10 mL) was kept at room temperature for 4 days to give triazoline **8b** (0.45 g, 24%): mp 117 °C (recrystallized from ether); ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 3 H), 1.75 (d, 3 H, $J = 1.1$ Hz), 1.82 (s, 3 H), 2.56 (d, 1 H, $J = 17$ Hz), 3.34 (d, 1 H, $J = 1.3$ Hz), 3.66 (d, 1 H, $J = 17$ Hz), 6.23 (br s, 1 H), 6.96 (t, 1 H, $J = 7.5$ Hz), 7.14–7.27 (m, 2 H), 7.65 (d, 1 H, $J = 7.5$ Hz); IR (Nujol) 1679, 1162 cm^{-1}; UV (MeOH) λ_{max} 206 nm (ϵ 37 900), 226 (35 300), 274 (8800), 332 (11 100); mass spectrum, m/e (relative intensity) 239 ($M^+ - 28$) (0.79), 196 (100).

Anal. Calcd for $C_{16}H_{17}ON_3$: C, 71.88; H, 6.41. Found: C, 71.96; H, 6.38.

Thermolysis of Triazoline 8a. A. 2-Aza-6,8-dimethyl-10-*tert*-butyl-3,4-benzotricyclo[4.4.0.0^{2,8}]dec-8-en-7-one (9a). A suspension of **8a** (85 mg, 0.27 mmol) in benzene–Decalin (1:1, 6 mL) was heated at 150 °C under nitrogen for 5 min with stirring. The resulting solution was concentrated (bath temperature 70 °C) and the residue was purified via flash chromatography (silica gel; ethyl acetate–hexane 1:4) and preparative TLC (silica gel; ether–hexane 1:4; R_f 0.6) to give aziridine **9a** (69 mg, 89%); mp 129–131 °C (recrystallized from petroleum ether): ^{1}H NMR ($CDCl_3$) δ 1.13 (s, 9 H), 1.43 (s, 3 H), 1.43 (s, 3 H), 2.71 (d, 1 H, $J = 13.8$ Hz), 2.75 (d, 1 H, $J = 13.8$ Hz), 3.01 (d, 1 H, $J = 1.2$ Hz), 6.36 (m, 1 H), 6.76–6.98 (m, 3 H), 7.02–7.16 (m, 1 H); IR ($CDCl_3$) 1662, 1248 cm^{-1}; UV (MeOH) λ_{max} 208 nm (ϵ 13 500), 232 (12 600), 322 (1240).

Anal. Calcd for $C_{19}H_{23}ON$: C, 81.10; H, 8.24; N, 4.98. Found: C, 80.63; H, 8.23; N, 5.15.

B. 2-Aza-6,8-dimethyl-10-*tert*-butyl-3,4-benzotricyclo[4.4.0.0^{2,8}]dec-9-en-7-one (10a). A suspension of **8a** (12 mg, 0.038 mmol) in Decalin (1 mL) was heated (150 °C) for 5 min under nitrogen. Cooling to room temperature and filtration gave crystalline **10a** (9 mg, 82%): mp 150–152 °C; ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9 H), 1.21 (s, 3 H), 1.25 (s, 3 H), 2.86 (d, 1 H, $J = 18$ Hz), 2.92 (d, 1 H, $J = 18$ Hz), 3.95 (d, 1 H, $J = 1.8$ Hz), 5.68 (d, 1 H, $J = 1.8$ Hz), 7.10 (s, 4 H); IR ($CDCl_3$) 1739, 1261, 833 cm^{-1}; UV (MeOH) λ_{max} 211 nm (ϵ 12 100), 324 (400).

Anal. Calcd for $C_{19}H_{23}ON$: C, 81.10;, H, 8.24. Found: C, 81.00; H, 8.28.

Thermolysis of Triazoline 8b. A. 2-Aza-6,8,10-trimethyl-3,4-benzotricyclo[4.4.0.0^{2,8}]dec-8-en-7-one (9b). A solution of **8b** (123 mg, 0.461 mmol) in benzene (12 mL) was heated (65 °C) for 75 min and concentrated to afford a yellow oil (117 mg). A portion (44 mg) of the oil was chromatographed (alumina; ether–hexane 4:1; R_f 0.3) to give pure aziridine **9b** (oil, 29 mg, 70%), which was generally converted to **10b** (vide infra) to prevent decomposition: ^{1}H NMR ($CDCl_3$) δ 1.43 (d, 3 H, $J = 1.5$ Hz), 1.45 (s, 3 H), 1.66 (s, 3 H), 2.70 (d, 1 H, $J = 14$ Hz), 2.76 (d, 1 H, $J = 14$ Hz), 2.86 (d, 1 H, $J = 1.2$ Hz), 6.16 (t, 1 H, $J = 1.4$ Hz), 6.78–7.00 (m, 3 H), 7.03–7.16 (m, 1 H); IR (film) 1662, 1238 cm^{-1}; UV (MeOH) λ_{max} 209 nm (ϵ 11 600), 229 (12 300), 313 (1570).

B. 2-Aza-6,8,10-trimethyl-3,4-benzotricyclo[4.4.0.0^{2,8}]dec-9-en-7-one (10b). A suspension of **8b** (376 mg, 1.41 mmol) in Decalin (5 mL) was heated (150 °C) for 5 min and concentrated to give a yellow oil. VPC analysis (200–220 °C) of the oil showed the presence of **10b** (1.3 min, 93%) and **11** (2.3 min, 7%). The oil was flash chromatographed (silica gel; ethyl acetate–hexane 1:4) to give crystalline **10b** (289 mg, 86%): mp 72–74 °C; ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 3 H), 1.27 (s, 3 H), 2.04 (d, 3 H, $J = 1.5$ Hz), 2.88 (s, 2 H), 3.74 (br s, 1 H), 5.73 (m, 1 H), 7.12 (m, 4 H); IR (film) 1741, 1262, 824 cm^{-1}; mass spectrum, m/e (relative intensity) 239 (M^+)(8.38), 178 (37.7), 167 (70.1), 115 (71.2), 77 (100); UV (MeOH) λ_{max} 212 nm (ϵ 12 300), 319 (410).

Anal. Calcd for $C_{16}H_{17}ON$: C, 80.30; H, 7.16. Found: C, 80.29; H, 7.09.

Thermolysis of Aziridine 9a. A suspension of **9a** (78 mg, 0.28 mmol) in Decalin (5 mL) was heated (150 °C) for 15 min. After evaporation of solvent (42 °C (1.2 mmHg)) pure, crystalline **10a** (78 mg, 100%) was obtained.

Thermolysis of Aziridine 9b. A suspension of **9b** (19 mg, 0.08 mmol) in Decalin (1 mL) was heated for 5 min and concentrated to give a yellow oil. VPC analysis (200–220 °C) of the oil showed the presence of **10b** (90%) and **11** (7%). The oil was chromatographed (silica gel; ether–hexane, 4:1 R_f 0.3) to afford pure **10b** (14 mg, 74%).

Photolysis of Triazoline 8a. A. Using the Pyrex Filter. A solution of **8a** (13 mg, 0.04 mmol) in THF–methanol (1:2, 15 mL) was irradiated for 60 min and concentrated to give a yellow oil (13 mg), which was chromatographed (silica gel; ether–hexane 1:19; R_f 0.3) to give **12a** (11 mg, 85%): ^{1}H NMR ($CDCl_3$) δ 1.01 (d, 3 H, J = 7 Hz), 1.25 (s, 9 H), 1.95 (m, 3 H), 2.20–3.00 (m, 3 H), 5.95 (m, 1 H), 6.37 (d, 1 H, J = 2 Hz), 7.25–7.35 (m, 4 H); IR (film) 1738, 1498, 774, 745 cm^{-1}.

Anal. Calcd for $C_{20}H_{27}O_2N$: C, 76.64; H, 8.68. Found: C, 76.82; H, 8.59.

B. Using the 366-nm Light Source. A solution of **8a** (19 mg, 0.06 mmol) in THF–methanol (5:1, 30 mL) was irradiated for 60 min and concentrated to give crystalline material (17 mg). ^{1}H NMR and VPC analysis (200–220 °C) of the crystalline material showed the presence of **10a** and a small amount of pyrrole ester **12a** (~10%).

Photolysis of Triazoline 8b. A. Using the Pyrex Filter. A solution of triazoline (19 mg, 71 mmol) in THF–methanol (1:2, 15 mL) was irradiated for 30 min and concentrated to give yellow crystalline material (18 mg), which was chromatographed (silica gel; ethyl acetate–hexane 1:9; R_f 0.3) to give pure dienone **11** (13 mg, 75%): mp 153–154 °C; ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 3 H), 1.86 (d, 3 H, J = 1 Hz), 2.40 (d, 1 H, J = 16 Hz), 3.15 (d, 1 H, J = 16 Hz), 4.03 (br s, 1 H), 5.35 (s, 1 H), 5.42 (s, 1 H), 6.50 (d, 1 H, J = 9 Hz), 6.63 (t, 1 H, J = 8 Hz), 6.87 (s, 1 H), 6.92–7.04 (m, 2 H); IR (Nujol) 3336, 1659, 1300, 1270, 916, 742 cm^{-1}; mass spectrum, m/e (relative intensity) 239 (M$^+$)(87.5), 224 (63.3), 196 (53.2), 144 (100), 130 (56.8); UV (MeOH) λ_{max} 255 nm (ε 12 800), 272 (13 000).

Anal. Calcd for $C_{16}H_{17}ON$: C, 80.30; H, 7.16. Found: C, 80.16; H, 7.27.

B. Using the 366-nm Light Source. A solution of **8b** (21 mg, 79 mmol) in methanol (24 mL) was irradiated for 60 min and concentrated to give crystalline material (19 mg). ^{1}H NMR and VPC analysis showed the presence of **10b** and **11** (ratio of **11**/**10b** = 3).

Photolysis of Aziridine 9a. A. Using the Pyrex Filter. A solution of **9a** (30 mg, 110 mmol) in THF–methanol (1:2, 15 mL) was irradiated for 60 min and concentrated to afford an oil (22 mg). VPC analysis (120–250 °C) of the oil showed the presence of **12a** (6 min, 77%). The oil was chromatographed (silica gel; ethyl acetate–hexane 1:9; R_f 0.6) to give the pyrrole **12a** (13 mg, 37%).

B. Using the 366-nm Light Source. A solution of **9a** (19 mg, 0.06 mmol) in methanol (30 mL) was irradiated for 70 min and concentrated to give crystalline material (18 mg). ^{1}H NMR of the crystals showed the presence of **10a** and a trace amount of pyrrole **12a**.

Photolysis of Aziridine 9b. A solution of **9b** (27 mg, 0.11 mmol) in methanol (17 mL) was irradiated for 90 min and concentrated to give yellow crystalline material, which was chromatographed (silica gel; ethyl acetate–hexane 1:9, R_f 0.3) to give pure **11** (12 mg, 44%).

Photolysis of Amine 10a. A solution of **10a** (9 mg, 32 mmol) in methanol (14 mL) was irradiated for 60 min with a Pyrex filter and concentrated to give an oil (9 mg). ^{1}H NMR and VPC analysis (200–220 °C) of the oil showed the presence of **12a** (73%).

Photolysis of Amine 10b. A solution of amine **10b** (111 mg, 0.42 mmol) in methanol (250 mL) was irradiated for 40 min and concentrated to give an oil, which was chromatographed (silica gel; ethyl acetate–hexane 1:4; R_f 0.7) to give **12b** (61 mg, 46%): ^{1}H NMR ($CDCl_3$) δ 1.02 (d, 3 H, J = 6 Hz), 1.96 (s, 3 H), 2.13 (s, 3 H), 2.4–3.0 (m, 3 H), 3.59 (s, 3 H), 5.90 (m, 1 H), 6.40 (m, 1 H), 7.00–7.70 (m, 4 H); IR (film) 1738, 1496, 783, 755 cm^{-1}; mass spectrum, m/e (relative intensity) 271 (M$^+$) (75.5), 212 (95.8), 196 (100), 168 (98.6).

3-(*N*-Benzylanilino)cyclohex-2-en-1-one (14a). To a suspension of 1,3-cyclohexanedione (93 g, 0.8 mmol) in benzene (1.4 L) was added *N*-benzylaniline (93 g, 0.5 mmol) and *p*-toluenesulfonic acid (5 g). The mixture was heated to reflux in a Dean-Stark apparatus for 20 h. After cooling, the solution was washed with 1 N sodium hydroxide (3 × 300 mL), water (3 × 300 mL), and brine (2 × 300 mL). Drying ($MgSO_4$), concentration, and distillation (200–220 °C (0.008 mmHg)) gave **14a** (136 g, 98%): ^{1}H NMR ($CDCl_3$) δ 1.67–2.50 (m, 6 H), 4.78 (s, 2 H), 5.35 (s, 1 H), 6.88–7.50 (m, 5 H); IR ($CHCl_3$) 3000, 1615, 1550 cm^{-1}; mass spectrum, m/e 277 (M$^+$).

Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90. Found: C, 82.20; H, 6.45.

3-(*N*-Benzylanilino)-6-ethylcyclohex-2-en-1-one (14b). To a solution of lithium diisopropylamide (198 mmol), which was prepared from diisopropylamine (30 mL), THF (180 mL), and *n*-butyllithium (2.18 M in hexane, 94 mL), was added HMPA (35.3 mL) at −78 °C. After stirring for 30 min, a solution of **14a** (50 g, 180 mmol) in THF (500 mL) was slowly added at −78 °C over a period of 2 h. The reaction mixture was stirred at −78 °C for 30 min and ethyl iodide (43.3 mL, 540 mmol) was added in one portion at −78 °C. The mixture was stirred at −78 °C for 5 h, allowed to warm to room temperature, and stirred for an additional 15 h. Saturated sodium bicarbonate (600 mL) was added and the reaction mixture was extracted with benzene (2 × 900 mL). The benzene layer was washed with water (500 mL) and brine (2 × 500 mL), dried ($MgSO_4$), and concentrated to give an oily product, which was chromatographed by preparative HPLC (ethyl acetate–hexane 1:1) to give **14b** (50 g, 91%): ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, J = 7.0 Hz), 1.20–2.50 (m, 7 H), 4.79 (s, 2 H), 5.31 (s, 1 H), 6.90–7.45 (m, 10 H); IR (film) 1620, 1550 cm^{-1}; mass spectrum, m/e 305 (M$^+$).

Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59. Found: C, 82.56; H, 7.60.

3-(*N*-Benzylanilino)-6-(3-chloropropyl)-6-ethylcyclohex-2-en-1-one (14c). To a solution of lithium diisopropylamide (205 mmol) in THF (100 mL) was added a solution of **14b** (45 g, 148 mmol) in THF (400 mL) and HMPA (30 mL) over a period of 2.5 h at −78 °C. The reaction mixture was stirred at −78 °C for 4.5 h, after which 1-bromo-3-chloropropane (70 g, 444 mmol) was added dropwise while the reaction temperature was kept below −60 °C. After stirring at −78 °C for 5 h the reaction was allowed to warm to room temperature and stirred for 15 h. The same workup procedure that was used for the preparation of **14b** followed by preparative HPLC (ethyl acetate–hexane 1:1) gave **14c** (39 g, 85% based on recovered **14b**, 8.4 g): ^{1}H NMR ($CDCl_3$) δ 0.81 (t, 3 H, J = 7.0 Hz), 1.20–1.90 (m, 8 H), 2.34 (t, 2 H, J = 6.0 Hz), 3.30–3.60 (m, 2 H), 4.78 (s, 2 H), 5.25 (s, 1 H), 6.95–7.40 (m, 10 H); IR (film) 1610, 1550 cm^{-1}; mass spectrum, m/e 383 (M$^+$ + 2), 381 (M$^+$).

3-Anilino-6-(3-chloropropyl)-6-ethylcyclohex-2-en-1-one (14d). To a solution of **14c** (44 g) in absolute ethanol (200 mL) and acetic acid (100 mL) was added a suspension of palladium catalyst (5% on activated carbon, 9 g) in acetic acid (20 mL). The mixture was hydrogenated on a Parr hydrogenator under 35 psi for 15 h. After filtration of the reaction mixture through Celite, the solvent was removed and the residue was dissolved in chloroform (150 mL). The solution was washed with 1 N sodium carbonate solution (2 × 150 mL) and brine (150 mL). After drying ($MgSO_4$), the solution was concentrated to give the crude product. Preparative HPLC (ethyl acetate–hexane 1:1) gave **14d** (21 g, 63%): ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3 H, J = 7.0 Hz), 1.10–2.20 (m, 8 H), 3.30–3.62 (m, 2 H), 3.50 (t, 2 H, J = 6.0 Hz), 5.38 (s, 1 H), 6.90–7.40 (m, 5 H), 7.50 (br s, NH); IR ($CHCl_3$) 1605, 1590 cm^{-1}; chemical ionization mass spectrum, m/e 292 (M$^+$ + 1).

6-(3-Chloropropyl)-6-ethyl-3-(*N*-(methoxycarbonyl)anilino)cyclohex-2-en-1-one (14e). To a solution of **14d** (18.9 g, 65 mmol) in THF (400 mL) was added *n*-butyllithium (2.4 M in hexane, 27.8 mL) dropwise at −78 °C. After stirring at −78 °C for 20 min, methyl chloroformate (10 mL, 130 mmol) was added in five equal portions. The mixture was allowed to stir at −78 °C for 1 h, warmed to room temperature, and stirred for 2 h. The solvent was removed and the residue was dissolved in a mixture of dichloromethane and ether (1:1, 200 mL). The solution was washed with water (2 × 100 mL) and brine (100 mL), dried ($MgSO_4$), and concentrated to give crude **14e** (22.5 g, 100%): ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3 H, J = 7.0 Hz), 1.22–2.10 (m, 8 H), 2.82 (t, 2 H, J = 6.0 Hz), 3.30–3.65 (m, 2 H), 3.70 (s, 3 H), 5.35 (s, 1 H), 6.95–7.50 (m, 5 H); IR ($CHCl_3$) 1725, 1640, 1600 cm^{-1}; chemical ionization mass spectrum, m/e 352 (M$^+$ + 2), 350 (M$^+$).

6-(3-Azidopropyl)-6-ethyl-3-(*N*-(methoxycarbonyl)anilino)cyclohex-2-en-1-one (15a). To a solution of **14e** (crude, 22.5 g, 65 mmol) in dry DMF (150 mL) was added sodium azide (4.94 g, 76 mmol). The resulting mixture was stirred and heated at 80 °C for 12 h. The solvent was removed on a rotary evaporator equipped with a mechanical vacuum pump. The residual oil was dissolved in a mixture of ether (150 mL) and dichloromethane (50 mL), and the resulting solution was washed with water (3 × 100 mL) and brine (100 mL). After drying ($MgSO_4$), the solution was concentrated to give crude **15a** (21 g, 90%): ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 2 H, J = 6.0 Hz), 3.08–3.40 (m, 2 H), 3.70 (s, 3 H), 5.30 (s, 1 H), 6.95–7.50 (m, 5 H); IR (film) 2090, 1725, 1640 cm^{-1}; mass spectrum, m/e 328 (M$^+$ − 28).

6-(3-Azidopropyl)-4-bromo-6-ethyl-3-(*N*-(methoxycarbonyl)anilino)cyclohex-2-en-1-one (15b). To a solution of crude **15a** (3.89 g, 11.0 mmol) in carbon tetrachloride (50 mL) was added *N*-bromosuccinimide (2.35 g, 13.2 mmol) and azobis(isobutyronitrile) (2 mg). The reaction mixture was heated to reflux for 1 h. After cooling to room temperature the precipitate was removed by filtration and the solution was washed with 5% sodium thiosulfate (20 mL), water (20 mL), and brine (20 mL). After drying ($MgSO_4$), the solution was concentrated to give an oil. Preparative HPLC gave **15b** (3.3 g, 69%): ^{1}H NMR ($CDCl_3$) δ 0.60–1.10 (m, 3 H), 1.20–2.40 (m, 6 H), 2.53 (d, 2 H, J = 6.0 Hz), 3.10–3.40 (m, 2 H), 3.72 (s, 3 H), 5.42 (d, 1 H, J = 2.0 Hz), 5.90 (t, 1 H, J = 6.0 Hz), 7.00–7.60 (m, 5 H); IR (film) 2090, 1700, 1650 cm^{-1}; chemical ionization mass spectrum, m/e 437 (M$^+$ + 2), 435 (M$^+$).

6-(3-Azidopropyl)-6-ethyl-3-(*N*-(methoxycarbonyl)anilino)cyclohex-2,4-dien-1-one (16a). To a solution of **15b** (15 g, 34 mmol) in acetone (200 mL) was added tetraethylammonium acetate (14.7 g, 78 mmol). The reaction mixture was heated to reflux for 1 h. Filtration and concentration gave an oil. Preparative HPLC (ethyl acetate–hexane; 1:1) gave **16a** (9.5 g, 79%): ^{1}H NMR (CDCl$_3$) δ 0.74 (t, 3 H, J = 7.0 Hz), 1.10–2.30 (m, 6 H), 3.00–3.40 (m, 2 H), 3.80 (s, 3 H), 5.70 (d, 1 H, J = 2.0 Hz), 6.22 (d, 1 H, J = 9.0 Hz), 6.80 (dd, 1 H, J = 9.0 Hz and 2.0 Hz), 7.05–7.60 (m, 5 H); IR (CHCl$_3$) 2090, 1725, 1640 cm^{-1}; UV (MeOH) λ_{max} 324 nm (ε 9200), 261 (7500), 222 (17 800), 204 (21 600).

6-(3-Azidopropyl)-6-ethyl-3-anilinocyclohex-2,4-dien-1-one (16b). To a solution of **16a** (136 mg, 0.384 mmol) in dry methanol (8 mL) was added sodium hydride (20 mg, 0.83 mmol) in several portions at 0 °C. The reaction mixture was stirred at room temperature for 2.5 h. After cooling to 0 °C, saturated ammonium chloride solution (3 mL) was added to the reaction mixture. The mixture was extracted with chloroform (3 × 10 mL) and the combined chloroform solution was washed with brine (2 × 10 mL). After drying (MgSO$_4$), the solvent was removed and the residue was chromatographed by preparative TLC (silica gel, ethyl acetate) to give **16b** (56 mg, 49%): ^{1}H NMR (CDCl$_3$) δ 0.70 (t, 3 H, J = 7.0 Hz), 1.10–2.40 (m, 6 H), 2.95–3.33 (m, 2 H), 5.70 (br s, 2 H), 7.00–7.45 (m, 5 H), 7.70 (br s, 1 H); IR (CHCl$_3$) 2100, 1650 cm^{-1}.

6a-Ethyl-5,6,6a,7,9a,9b-hexahydro-9-(*N*-(methylcarbonyl)anilino)-7-oxo-4*H*-1,2,3-triazolo[4,5,1-*ij*]quinoline (17a). Method A. A solution of **16a** (268 mg, 0.757 mmol) in benzene (25 mL) was heated to reflux for 3.5 h. Concentration and preparative TLC gave **17a** (179 mg, 67%).

Method B. A neat sample of **16a** (5 g, 14.1 mmol) was placed in a round-bottom flask and heated at 100–120 °C for 25 min; the sample was agitated by shaking occasionally. After cooling, the sample was recrystallized from ether to give **17a** (2 g); mp 164–165 °C. The mother liquor was concentrated and chromatographed by preparative HPLC (ethyl acetate–hexane 1:1) to yield **17a** (1.1 g, total yield 3.1 g, 62%). ^{1}H NMR (CDCl$_3$) δ 0.81 (t, 3 H, J = 7.0 Hz), 1.02–2.80 (m, 6 H), 3.17 (d, 1 H, J = 10 Hz), 3.73 (s, 3 H), 3.99–5.45 (m, 2 H), 5.28 (s, 1 H), 6.40 (d, 1 H, J = 10 Hz), 6.90–7.50 (m, 5 H); IR (CHCl$_3$) 1725, 1660 cm^{-1}; mass spectrum, m/e 354 (M$^+$), 326 (M$^+$ – 28); UV (MeOH) λ_{max} 286 nm (ε 11 800), 268 (11 200), 242 (13 000).

Anal. Calcd for $C_{19}H_{22}N_4O_3$: C, 64.39; H, 6.26; N, 15.81. Found: C, 64.40; H, 6.28; N, 15.76.

Preparation of Compound 17b. A solution of **16b** (140 mg, 0.473 mmol) in benzene (10 mL) was heated to reflux for 5 h. Concentration preparative TLC (ethyl acetate) gave **17b** (102 mg, 73%): mp 181–182 °C; ^{1}H NMR (CDCl$_3$) δ 0.82 (t, 3 H, J = 7.0 Hz), 1.20–2.20 (m, 6 H), 2.50–3.20 (m, 1 H), 3.38 (d, 1 H, J = 10 Hz), 4.05–4.50 (m, 1 H), 5.35 (d, 1 H, J = 10 Hz), 5.75 (s, 1 H), 7.00–7.60 (m, 5 H), 8.05 (br s, 1 H); IR (CHCl$_3$) 3200, 1605, 1590 cm^{-1}; UV (MeOH) λ_{max} 316 nm (ε 16 900), 236 (13 100), 225 (13 800), 205 (13 000).

Anal. Calcd for $C_{17}H_{20}N_4O$: C, 68.90; H, 6.80; N, 18.90. Found: C, 68.90; H, 6.82; N, 18.84.

Photolysis of 17a (Methanol Solution). Triazoline **17a** (40 mg, 0.11 mmol) in methanol (3 mL) was irradiated and worked up as described for preparation of **6a**. Chromatography (silica gel, ethyl acetate) gave **18** (30 mg, 75%): ^{1}H NMR (CDCl$_3$) δ 0.82 (t, 3 H, J = 7.0 Hz), 1.05–2.40 (m, 8 H), 3.67 (s, 3 H), 3.72 (s, 3 H), 3.50–3.90 (m, 1 H), 5.83 (m, 1 H), 6.45 (m, 1 H), 6.62 (m, 1 H), 7.15–7.40 (m, 5 H); IR (CHCl$_3$) 1710 cm^{-1}; chemical ionizaiton mass spectrum, m/e 359 (M$^+$ + 1).

Photolysis of 17a (Benzene Solution). A solution of **17a** (70 mg, 0.14 mmol) in spectrophotometric grade benzene (3 mL) was irradiated with Pyrex-filtered light for 30 min. Removal of solvent gave the ketene dimer (65 mg): ^{1}H NMR (CDCl$_3$) δ 0.92 (t, 6 H, J = 7.0 Hz), 1.00–2.90 (m, 12 H), 3.70 (s, 6 H), 3.50–4.10 (m, 4 H), 5.70–5.95 (m, 2 H), 6.31–6.50 (m, 2 H), 6.55–6.70 (m, 2 H), 7.10–7.55 (m, 10 H); IR (CHCl$_3$) 1810, 1710 cm^{-1}; chemical ionization mass spectrum, m/e 653 (M$^+$ + 1); ^{13}C NMR (CDCl$_3$) δ 215 (carbonyl carbon of the cyclobutane-1,3-dione ring system).

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Synthesis of a Dodecahydro-18,21-dioxoniakekulene

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Abstract: The synthesis of 1,2,4,5,7,8,10,11,13,14,24,25-dodecahydro-18,21-dioxonia-15,23:16,22-dimethenobenzo[1,2-*a*:5,4-*a'*]dipentaphene bis(trifluoromethanesulfonate) (**18**) is described. The key intermediate, 3,4,6,7,9,10-hexahydropentaphene-1,12(2*H*,11*H*)-dione (**6**), is prepared in seven steps from 9,10-dihydrophenanthrene in 32% yield via a double-Haworth synthesis. A Vilsmeier–Haack reaction on pentaphenedione **6** afforded 1,12-dichloro-3,4,6,7,9,10-hexahydro-2,11-pentaphenedicarboxaldehyde (**17**), which was condensed with pentaphenedione **6** in a convergent synthesis to afford the novel macrocyclic salt **18**. Spectral properties and transformations of macrocycle **18** are discussed.

The synthesis of macrocycles containing cavities solely on account of benzenoid ring fusion is a challenging and little-explored area of organic chemistry; hydrocarbons of this form have been referred to as "coronaphenes".[1] The a priori possibilities of annulenoid vs. benzenoid aromaticity render these macrocycles of considerable theoretical interest.[2] Questions regarding the ring strain resulting from polynuclear condensation and strain imposed by internal nonbonding interactions also arise.

Kekulene **1**, synthesized by Diederich and Staab,[3] represents the first and so far only example of a coronaphene. The minimal amount of angle strain and small nonbonding interactions in hydrocarbon **1** appeared to make attractive syntheses of heterokekulenes such as **2** and **4**.

We sought to develop an accessible route to heterokekulenes, with the possibility of converting bispyrylium salt **2** into hydrocarbon **1** via the known transformations of pyrylium salts into arenes.[4-7] A flexible route to diazakekulene **4** would allow the introduction of substituents and the testing of macrocycle **4** as a possible ligand for cations.[8]

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