

Photochemistry of Trans-Fused Bicyclo[4.*n*.0] 2,4-Dienes. Ground-State Conformational Control in Rigid Systems¹

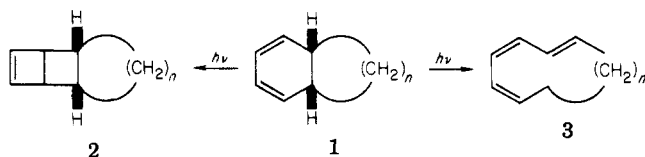
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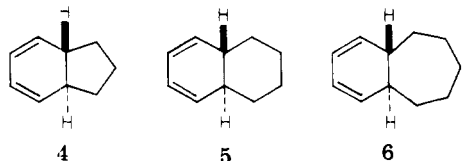
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The photochemistry of a series of simple trans-fused bicyclo[4.*n*.0] 2,4-dienes (*n* = 3, 4, 5) which possess semirigid structures in the ground state has been studied. *trans*-Bicyclo[4.3.0]nona-2,4-diene gave rise to *cis,cis,cis*-cyclonona-1,3,5-triene, the first example of a nonaccordant cyclohexadiene ring opening. The *trans*-bicyclo[4.4.0]deca-2,4-diene at -40 °C, using 254-nm light, yielded *trans,cis,trans*-cyclodeca-1,3,5-triene. This triene upon further irradiation yielded *endo,endo*-tricyclo[5.3.0.0^{2,10}]dec-8-ene. The triene was extremely thermally labile and was readily converted to *cis*-bicyclo[4.4.0]deca-2,4-diene. At -78 °C, the photostationary state of *trans*-bicyclo[4.4.0]deca-2,4-diene showed a wavelength dependency. The photochemistry of *trans*-bicyclo[5.4.0]undeca-8,10-diene was analogous to that of the ten-carbon analogue.

The photochemistry of the conformationally mobile *cis*-fused bicyclo[4.*n*.0] 2,4-dienes (1) has been shown to be subject to "ground-state conformational control."² These dienes upon photochemical activation either close to bicyclo[2.2.0]hex-2-enes (2) or open to trienes (3). The



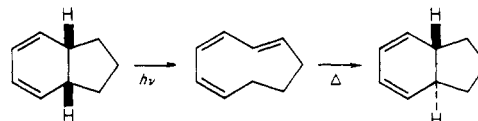
product ratio in such a photochemical process has been shown to be dependent on the population of the various lower energy ground-state conformations. This present study was undertaken to evaluate the role of ground-state conformational control in the more rigid *trans*-fused bicyclo[4.*n*.0] 2,4-dienes 4-6.



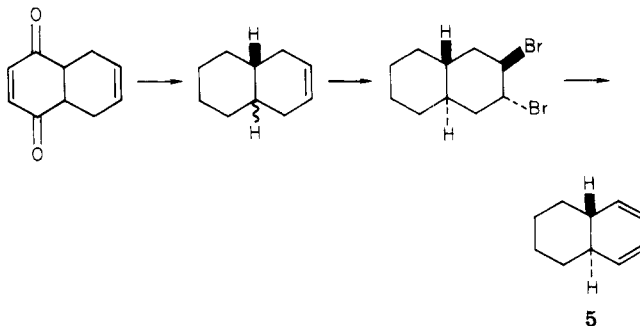
Synthesis

The synthesis of *trans*-bicyclo[4.3.0]nona-2,4-diene (4) was achieved by thermal ring closure of *trans,cis,cis*-cyclonona-1,3,5-triene which, in turn, was prepared by

ultraviolet irradiation of *cis*-bicyclo[4.3.0]nona-2,4-diene.²



The synthesis of *trans*-bicyclo[4.4.0]deca-2,4-diene (5) was based on a scheme previously reported.³ The enedione system of the 1,3-butadiene-benzoquinone adduct was reduced and the resulting diketone was subjected to a Wolff-Kishner reduction to yield a mixture of *cis*- and *trans*- Δ^2 -octalins. This olefin mixture was brominated and the pure 2,3-dibromo-*trans*-decalin was obtained by fractional crystallization.⁴ This product was dehydrobrominated with potassium *tert*-butoxide in THF to give diene 5.



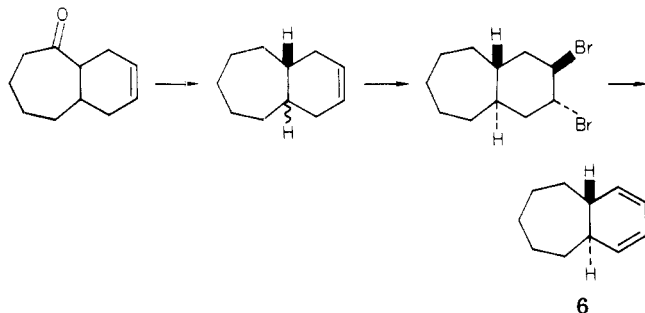
(1) This investigation was supported by Grant AM-00709, awarded by the National Institute of Arthritis, Metabolism, and Digestive Diseases, DHEW.

(2) Dauben, W. G.; Kellogg, M. S. *J. Am. Chem. Soc.*, **1980**, *102*, 4456.

(3) Mehrotra, K. N. *Diss. Abstr.* **1967** 6607353.

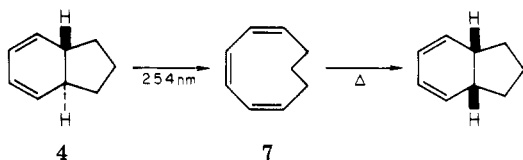
(4) Johnson, W. S.; Bauer, V. J.; Margrave, J. L.; Frisch, M. A.; Dreger, L. L.; Hubbard, W. N. *J. Am. Chem. Soc.* **1961**, *83*, 606.

A similar synthetic route was utilized to prepare *trans*-bicyclo[5.4.0]undeca-8,10-diene (6). The adduct from the aluminum chloride catalyzed addition of 1,3-butadiene to cycloheptenone upon Clemmensen reduction yielded a mixture of the *cis* and *trans* olefins. The *trans* dibromide was obtained by fractional crystallization and converted to diene 6.



Results

In an initial exploratory experiment, a pentane solution of *trans*-bicyclo[4.3.0]nona-2,4-diene (4) was irradiated at 254 nm under a nitrogen atmosphere at room temperature. A single product was rapidly formed and upon continued irradiation this primary irradiation product was transformed into two secondary products. In a preparative reaction run under the same conditions, the crude reaction mixture was stirred with aqueous silver nitrate and the crystalline adduct of *cis,cis,cis*-cyclonona-1,3,5-triene (7) was isolated. The known triene 7⁵ was obtained upon treatment of the silver salt with ammonium hydroxide. As reported,⁵ this triene upon heating yielded *cis*-bicyclo[4.3.0]nona-2,4-diene.



An initial exploratory irradiation (254 nm) at room temperature of *trans*-bicyclo[4.4.0]deca-2,4-diene (5) revealed the formation of a single primary photoproduct, followed by the formation of several secondary products. When a preparative irradiation (254 nm) was run at -40°C , a different reaction course was followed in that although the single primary photoproduct was formed, it did not give rise to any secondary products during the course of conversion of 50% of the starting material. At this point, the irradiation was interrupted and the reaction mixture allowed to stand in the dark at -78°C for 11 h. Upon resumption of irradiation, secondary photoproducts began to appear. The product mixture was separated by dry column chromatography⁶ on silver nitrate impregnated silica gel. The major product was identified as *cis*-bicyclo[4.4.0]deca-2,4-diene (8) and the predominant minor product was shown to be *endo,endo*-tricyclo[5.3.0.0^{2,10}]dec-8-ene (9), a known compound.⁷ The other trace products could not be identified.

The alteration of the course of the reaction and the isolation of *cis* diene 8 as a major product suggested the possibility that a highly thermally labile triene was the

primary photoproduct, a result found in related studies.^{8,9} In an attempt to trap this suspected triene, a pentane solution of diene 5 was irradiated (254 nm, -78°C) and the mixture first was reduced with diimide at -78°C and then further reduced by catalytic hydrogenation.¹⁰ The reaction mixture was analyzed on both polar and nonpolar analytical VPC columns and the major product was shown to have a retention time identical (coinjection) with that of cyclodecane.

The irradiation of diene 5 at liquid nitrogen temperature in a methylcyclohexane glass was performed in an attempt to observe the formation of the primary photoproduct by UV spectroscopy. The initial spectrum of the starting diene 5 displayed a pronounced fine structure at the low temperature of the experiment. The glass was irradiated with a low-pressure mercury resonance lamp (mainly 254 nm) and there developed an increase in optical density, as well as the appearance of new maxima at longer wavelengths (282, 290 (sh), and 310 nm) than the longest wavelength absorption of diene 5.

These longer wavelength absorptions suggested the formation of a conjugated triene in a conformation in which there was good overlap of the π -system of the double bonds. The wavelength dependence of the photostationary state, a feature found in a related diene,¹¹ was demonstrated by irradiation of a pentane solution of diene 5 with 254-nm light at -78°C until the photostationary ratio of diene 5 to the elusive triene 10 (detected by VPC as the *cis* diene 8) was 0.5 to 1. The irradiation lamps were then replaced with Rayonet RPR-3000-A lamps (maximum output near 300 nm) and the irradiation was continued at this longer wavelength. The ratio of diene 5 to triene 10 increased to 5 to 1 and thereafter remained unchanged upon further 300 nm irradiation. No secondary photoproducts were detected in this irradiation study.

In order to obtain an IR spectrum of triene 10, diene 4 was irradiated (254 nm) in an argon matrix at 12 K. New absorbances, of moderate intensity, at 990, 978, and 954 cm^{-1} appeared, suggesting the presence of a symmetrically disubstituted *trans* double bond in the new photoproduct. In a control experiment argon matrix isolated *cis*-bicyclo[4.3.0]nona-2,4-diene was irradiated at 14 K with 254-nm light. It is known¹¹ that in solution this diene is transformed into *trans,cis,cis*-cyclonona-1,3,5-triene which showed out-of-plane C-H bonding modes at 975, 960, and 940 cm^{-1} . In the argon matrix bands at 978 and 964 cm^{-1} developed and when the wavelength of irradiation was changed to 300 nm the bands disappeared. Such spectral results agree with the expected wavelength dependency of the irradiation of this cyclononadiene derivative.¹¹

On the basis of the foregoing studies and upon consideration of orbital-symmetry concepts, the primary triene photoproduct 10 from diene 5 is assigned the structure *trans,cis,trans*-cyclodeca-1,3,5-triene. Further evidence for this assignment is found in the extremely facile thermal reaction of the triene 10 to *cis*-bicyclo[4.4.0]deca-2,4-diene (8).

The photochemistry of *trans*-bicyclo[5.4.0]undeca-8,10-diene (6) was found to be analogous to that reported above for the ten-carbon analogue. At room temperature,

(5) Glass, D. S.; Watthey, J. W. W.; Winstein, S. *Tetrahedron Lett.* 1965, 377.

(6) Loev, B.; Bender, P. E.; Smith, R. *Synthesis* 1973, 1972. Loev, B.; Goodman, M. M. *Chem. Ind.* 1967, 2026.

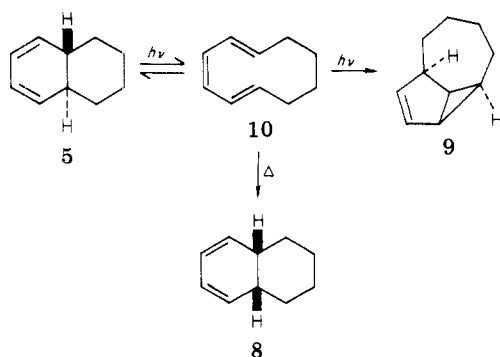
(7) Dauben, W. G.; Kellogg, M. S.; Seeman, J. I.; Vietmeyer, N. D.; Wendschuh, P. H. *Pure Appl. Chem.* 1973, 33, 197.

(8) Corey, E. J.; Hortmann, A. G. *J. Am. Chem. Soc.* 1965, 87, 5736. Miyashita, M.; Uda, H.; Yoshikoshi, A. *J. Chem. Soc. D* 1969, 1396. Watanabe, M.; Yoshikoshi, A. *J. Chem. Soc., Chem. Commun.* 1972, 698.

(9) Dauben, W. G.; Williams, R. G.; McKelvey, R. D. *J. Am. Chem. Soc.* 1973, 95, 3932.

(10) The failure of diimide to reduce certain double bonds in a closely related system has been reported (van Tamelen, E. E.; Burkoth, T. L.; Greeley, R. H. *J. Am. Chem. Soc.* 1971, 93, 6120) and catalytic hydrogenation was also used to complete the reduction.

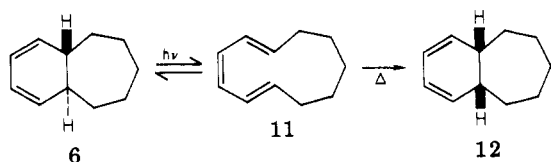
(11) Dauben, W. G.; Kellogg, M. S. *J. Am. Chem. Soc.* 1971, 93, 3805.



using 254-nm light, with reaction course being followed by VPC, one primary product and several secondary products were formed. The pattern of secondary product formation as well as the VPC retention times of all the components of the mixture was identical with those formed in the photochemistry of the corresponding *cis*-bicyclo[5.4.0]undeca-8,10-diene (12).² These results suggested, again, the possibility of the thermal rearrangement of an initial triene as reported above.¹²

When the photoreaction was repeated at -55 to -70 °C, no apparent reaction was detected by VPC analysis. An aliquot of the reaction mixture, taken after 4 h of irradiation, was shown to be an equal mixture of dienes 6 and 12 by IR and NMR analysis. As before, the cold reaction mixture was concentrated, reduced first with diimide, and then catalytically hydrogenated. The products were isolated by preparative VPC and shown to be *cis*-bicyclo[5.4.0]undecane and cycloundecane.

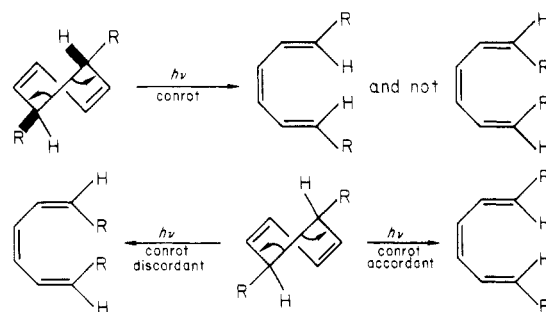
Thus, the major, if not the sole, primary photoproduct of diene 6 appears to be *trans,cis,trans*-cycloundeca-1,3,5-triene (11). This structural assignment is based upon the rapid formation of *cis* diene 12, thermally, and the facile photochemical closure to starting *trans* diene 6. Further study is needed to establish with certainty this conclusion.



Discussion

It has been proposed¹³ that 1,3-cyclohexadienes in which the diene moiety is planar react, preferentially, to form bicyclo[2.2.0]hex-2-enes, while those 1,3-cyclohexadienes in which the diene moiety is skewed react to form acyclic 1,3,5-hexatriene derivatives. Such selectivity in a photochemical process has been related to the "ground-state conformational control" in a photochemical reaction. Another example of ground-state conformational control has been termed the "accordant rule."¹⁴ This rule states that, of the two possible photochemically allowed conrotatory motions available to a skewed 1,3-cyclohexadiene undergoing a photochemical cleavage, the molecule will follow the motion which is "in accord with the chirality of the diene" (i.e., the least-motion pathway¹⁵).

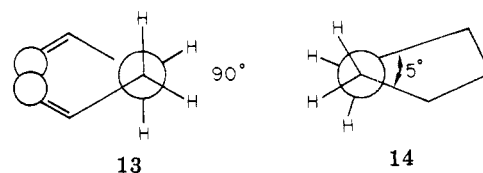
The ring opening results obtained with the 10- and 11-carbon diene systems 5 and 6 are consistent with both of



these postulates. In neither case was a bicyclo[2.2.0]hexene derivative detected; if formed at all, it must have an efficiency at least two orders of magnitude less than the ring opening. Similarly, although both *cis,cis,cis* and *trans,cis,trans* trienes are "allowed" according to orbital symmetry arguments,¹⁶ only *trans,cis,trans* trienes 10 and 11, which correspond to a ring opening "in accord with" the single skewed conformer allowed by the *trans*-fused bicyclic system, were detected.

The ring opening of the nine-carbon diene 4, however, yielded only the *cis,cis,cis* triene 7, the product resulting from a discordant conrotatory opening. This different reaction course cannot be attributed to steric hindrance in the accordant mode since *trans*-9,10-dimethylbicyclo[4.4.0]deca-2,4-diene, a compound with more potential steric hindrance, does open in accord with the helicity to give the *trans,cis,trans* isomer.

A more likely reason for this discordant opening arises from the angle strain inherent in the *trans*-bicyclo[4.3.0]nona-2,4-diene system, itself. The strain can best be seen by attempting to force a model of *cis,cis*-cyclonona-1,3-diene into the conformation of the bicyclic diene 4 by bringing C-5 and C-9 of the cyclononadiene into bonding distance. Considerable angle strain is generated during this maneuver. Indication of the strain is also found in the contrast between the "normal" 90° dihedral angle of the pseudoequatorial hydrogens of an unsubstituted 1,3-cyclohexadiene (13)¹⁷ with the 0–5° unstrained dihedral angle of cyclopentane (14).¹⁸ Fusion of two systems results in a large distortion from ideal geometries of each of the two separate rings.



Moreover, the strain is increased if the molecule is further distorted by an accordant ring opening. The discordant motion, on the other hand, results in a rapid decrease in angle strain of the developing cyclononatriene. This diene 4 is an example where the steric constraints override the electronic features on which the accordant ring-opening concept is based.

Conformational control is also demonstrated in the photochemistry of the *trans,cis,trans* trienes 10 and 11 by the predominance of the ring-closure reaction which yields dienes 5 and 6, respectively. Examination of molecular

(12) A mixture of authentic samples of *trans* diene 6 and *cis* diene 12 was inseparable by TLC, high-performance LC, or VPC on polar, non-polar, or capillary columns.

(13) Dauben, W. C.; Rabinowitz, J.; Vietmeyer, N. D.; Wendschuh, P. *H. J. Am. Chem. Soc.* 1972, 94, 4285.

(14) Baldwin, J. E.; Krueger, S. M. *J. Am. Chem. Soc.* 1969, 91, 6444.

(15) Tee, O. S.; Yates, K. *J. Am. Chem. Soc.* 1972, 94, 3074.

(16) (a) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970. (b) Dewar, M. J. S. *Tetrahedron Suppl.* 1966, 8, 75. (c) Zimmerman, H. E. *Acc. Chem. Res.* 1971, 4, 272.

(17) Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* 1972, 94, 5612.

(18) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; p 248.

models demonstrate that trienes **10** and **11** each have available to them a low-energy helical *s-cis,s-cis* conformation in which the terminal carbons of the triene are well positioned for a conrotatory closure. In fact, C-1,C-6 bonding via a conrotatory motion requires so little atomic displacement that the near exclusivity of the ring-closure pathway for the excited triene is easily understood. The helical conformation is also responsible for the great facility of the thermal ring closure, which requires only a slight rotation of C-1 and C-6 to bring the two carbon atoms within bonding distance in the disrotatory sense.

It is likely that this conformational effect is also responsible for the observed shift toward diene **5** of the photostationary state in the argon-matrix experiments, for the rigidity of the matrix would tend to contain the triene molecule to the conformation in which it was first formed. Although it has been observed¹⁹ that four rotamers of the light-induced ring-cleavage products of α -pyrone are formed in an argon matrix, the conformational mobility of triene **10** is inherently far more limited, and the motion of a large number of atoms in the matrix would be required for a change in conformation to occur. Thus it is likely that the rigidity of the matrix serves to maximize the efficiency of the photochemical ring closure.

Finally, the formation of *endo,endo*-tricyclo[5.3.0.0^{2,10}]dec-8-ene (**9**) as a photoproduct of trans diene **5** deserves comment. Since **9** has been reported² to be a possible product of the irradiation of cis diene **8**, it is tempting to postulate that **9** arose via a thermal cyclization of triene **10** to cis diene **8**. However, it is also reported,^{7,20} that in the irradiation of cis diene **8**, the 2-*exo*-7-*endo* isomer is formed with at least ten times the efficiency of **9**. Although in the present work, the workup conditions for the photoproducts of trans diene **5** were sufficiently mild to allow the isolation of the *exo,endo* isomer, none was detected. This result argues against cis diene **8** as a precursor of **9** in this present case.

Experimental Section

Infrared and NMR spectra were run with carbon tetrachloride as solvent unless otherwise noted. Combustion and mass spectral analyses were performed by the Analytical Laboratory, College of Chemistry, University of California, Berkeley.

The following columns were used for vapor-phase chromatography: A, 10 ft \times $\frac{1}{8}$ in., 10% Carbowax 600, 10% KOH on 60/80 G; B, 15 ft \times $\frac{1}{8}$ in., 10% SE-30 on 80/100 G; C, 6 ft \times $\frac{1}{8}$ in., 10% SE-30 on 80/100 S; D, 10 ft \times $\frac{1}{8}$ in., 4% SF-96 on 70/80 G; E, 10 ft \times $\frac{1}{8}$ in., 1% Carbowax 20M on 100/120 G.

trans-Bicyclo[4.3.0]nona-2,4-diene (**4**). A solution of 1.0 g (8.3 mmol) of *cis*-bicyclo[4.3.0]nona-2,4-diene² in 140 mL of pentane in a quartz reaction vessel was irradiated (0 °C, N₂ atmosphere) at 254 nm in a Rayonet reactor. Aliquots of the reaction mixture were withdrawn throughout the irradiation for analysis by VPC (column B, 100 °C). As soon as the photostationary state (*cis* diene-triene = 1:2) was reached, the solution was removed from the reactor and heated under reflux for 30 min. The solution was concentrated to a 10-mL volume by distillation of the pentane through a short column at atmospheric pressure and an ethereal solution of 0.5 g (10 mmol) of maleic anhydride added. The mixture was stirred at room temperature for 24 h and concentrated, the residue was dissolved in 10 mL of pentane, and the solution was filtered through a 5-cm column of silica gel. The solvent was removed to give 0.4 g (40%) of **4** in 87% purity by VPC analysis.

The separation of the *cis* and *trans* dienes could also be accomplished by preparative VPC (10 ft \times $\frac{3}{8}$ in., 10% Carbowax 6000, 10% KOH column, 150 °C) to give **4** in greater than 97%

purity in a yield of 72% based upon recovered *cis* starting material.

The following spectral and analytical data for *trans*-bicyclo[4.3.0]nona-2,4-diene are in agreement with the sparse data reported^{20,21} for this compound: UV_{max} (EtOH) 260 nm (ϵ 3950); IR (neat) 3012, 1698, 1613, 1447, 1107, 1053, 854, 676 cm⁻¹; NMR δ 0.8–2.5 (m, 8), 5.95 (m, 4); mass spectrum (70 eV), *m/e* 120 (25), 91 (100).

Anal. Calcd for C₉H₁₂: C, 89.94; H, 10.06. Found: C, 89.69; H, 10.29.

trans-Bicyclo[4.4.0]deca-2,4-diene (**5**). To a suspension of 7.0 g (62.5 mmol) of potassium *tert*-butoxide in 100 mL of dry THF, stirred rapidly under a nitrogen atmosphere, was added 2.30 g (10.7 mmol) of 2,3-dibromo-*trans*-decalin.^{3,4} The reaction mixture was stirred for 1 h at room temperature and poured into a separatory funnel containing 80 mL of pentane and 50 mL of water. The organic layer was washed (two 50-mL portions of water, one 50-mL portion of saturated NaCl solution) and dried (MgSO₄). The solvent was removed by distillation at atmospheric pressure, and the residue was distilled in a Kugelrohr apparatus (75 °C, 20 torr) to yield 1.093 g (76%) of **5** in greater than 98% purity by VPC: UV_{max} (EtOH) 262 nm (ϵ 3550); IR (neat) 3003, 1438, 968, 882, 844, 792, 682 cm⁻¹; NMR δ 0.7–2.2 (m, 10), 5.43–5.96 (m, 4); mass spectrum (70 eV), *m/e* 134 (57), 119 (39), 16 (33), 105 (57), 91 (100).

Bicyclo[5.4.0]undec-9-en-2-one. A stirred suspension of 2.93 g (22 mmol) of anhydrous AlCl₃ and 0.3 g (2.7 mmol) of hydroquinone in 150 mL of dichloromethane, contained in a 500-mL centrifuge bottle was purged with nitrogen and cooled to 0 °C. To this was added, dropwise, 12.13 g (110 mmol) of cycloheptenone and 33.3 g (6.17 mmol) of butadiene (dried by passage through molecular sieves (4-A) and condensed at -78 °C). The stopper was wired on and the reaction mixture was stirred at room temperature for 51 h and then transferred to a separatory funnel with 100 mL of carbon tetrachloride and 100 mL of 5% aqueous H₂SO₄ solution. The organic layer was washed with saturated NaCl solution and dried (MgSO₄). The solvent was removed and the residue was distilled to yield 8.26 g (46%) of bicyclo[5.4.0]undec-9-en-2-one: bp 80–84 °C (1.0 torr); IR (neat) 1695, 1645, 1439, 1172, 823 cm⁻¹; NMR δ 0.8–3.0 (m, 14), 6.50 (m, 2); mass spectrum (70 eV), *m/e* 164 (36), 135 (25), 79 (100).

Bicyclo[5.4.0]undec-9-ene. A solution of 5.14 g (31 mmol) of bicyclo[5.4.0]undec-9-en-2-one, 10 g (152 mmol) of KOH (85% pellets), and 11 g (187 mmol) of hydrazine hydrate (85%) in 50 mL of triethylene glycol, contained in a 250-mL flask under a nitrogen atmosphere, was heated to 150–200 °C (bath temperature) under gentle reflux for 1 h. The temperature was raised to 260 °C and the two-phase distillate collected began to show a yellow color. The distillate was extracted with ether, and the organic layer was dried (MgSO₄) and concentrated by rotary evaporation to yield 3.50 g (75%) of a mixture of *cis*- and *trans*-bicyclo[5.4.0]undec-9-ene. VPC analysis showed the mixture to be \geq 95% pure and the ratio of isomers to be 1:2. The mixture was not separated: IR (neat) 3058, 1456, 1439, 978 cm⁻¹; NMR δ 1.07–2.5 (m, 16), 5.48 (br s, 2).

9,10-Dibromo-*trans*-bicyclo[5.4.0]undecane. To a stirred solution of 3.10 g (20.6 mmol) of bicyclo[5.4.0]undec-9-ene (*cis,trans* mixture) in 25 mL of chloroform at 0 °C was added, dropwise, a solution of 3.40 g (21.3 mmol) of bromine in 25 mL of chloroform; a definite red-brown bromine color persisted in solution. The reaction mixture was washed with two 25-mL portions of 10% NaHSO₃ solution and two 25-mL portions of water and dried (MgSO₄). The solvent was removed by rotary evaporation to yield 5.93 g (93%) of crude dibromide. The material was recrystallized from hot methanol to yield 1.48 g of white solid, mp 48–51 °C, consisting of a single isomer by VPC. The subsequent dehydrohalogenation of this compound demonstrated that the ring juncture was *trans*: IR 1443, 1435, 1426, 1179, 954, 900 cm⁻¹; NMR δ 1.2–2.6 (m, 16), 4.65 (m, 2).

trans-Bicyclo[5.4.0]undeca-8,10-diene (**6**). To a stirred solution of 3.51 g (11.33 mmol) of *trans*-9,10-dibromobicyclo[5.4.0]undecane in 160 mL of dry THF was added 7.62 g (68 mmol) of freshly sublimed potassium *tert*-butoxide. The suspension was stirred for 50 min at room temperature and shaken with 75 mL

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(20) Alder, K. *Dortmann, H. Chem. Ber.* 1954, 87, 1905.

(21) Vogel, E.; Grimme, W.; Dinne, E. *Tetrahedron Lett.* 1965, 391.

of water and 105 mL of pentane in a separatory funnel. The organic layer was washed, dried (MgSO_4), and concentrated. The residue was distilled in a Kugelrohr apparatus (21 torr, 105–118 °C) to yield 1.40 g (84%) of **6** which possessed spectral properties in agreement with those previously reported.² The spectral data for this compound were similar to, but distinct from, those of the *cis* isomer. However, mixtures of the two isomeric dienes could not be separated by VPC on polar, nonpolar, or capillary columns.

Exploratory Irradiation of *trans*-Bicyclo[4.3.0]nona-2,4-diene (4) at Room Temperature (254 nm). A Vycor glass tube containing 4 mL of a 1.5×10^{-2} M stock solution of *trans*-bicyclo[4.3.0]nona-2,4-diene (**4**) in pentane was purged with nitrogen for 10 min, sealed with a serum stopper, and irradiated at 254 nm in the Rayonet reactor at ambient temperature (25–30 °C). Aliquots of the reaction mixture were removed periodically for analysis by VPC and by UV spectroscopy.

The course of the reaction was analyzed by VPC and it was found that there was a rapid decrease in the amount of starting material matched by an increase in a single product whose retention time matched that of *cis*-bicyclo[4.3.0]nona-2,4-diene. In addition, two other products of longer retention time appeared slowly. Upon continued irradiation, the initial product began to disappear, and the amounts of the secondary products increased.

Analysis of the course of the reaction by UV showed an initial decrease in the 260-nm maximum of the starting diene and a concurrent development of a new maximum at 296 nm. An approximate isobestic point at 255 nm was observed. Extended irradiation led to a decrease in the 296-nm maximum and an increase in optical density in the 220–250-nm region. At the end of the experiment, only end absorption was evident at wavelengths greater than 220 nm.

Preparative-Scale Irradiation of *trans*-Bicyclo[4.3.0]nona-2,4-diene (4). A solution of 300 mg of diene **4** in 140 mL of pentane was irradiated at 254 nm (Rayonet, 25–30 °C) for 1.5 h. The reaction solution was analyzed by VPC and it was found that most of the starting material had disappeared and a single major product had formed (>75%). The reaction mixture was concentrated (0 °C, reduced pressure) to 50 mL and stirred with 50 mL of a 50% aqueous solution of AgNO_3 for 1 h (dark). The aqueous layer was separated and treated with aqueous NH_3 solution until the initially formed AgOH precipitate redissolved. The solution was extracted with pentane (three 25-mL portions) and the combined pentane extracts were dried and concentrated under reduced pressure through a 14-cm Vigreux column to yield 150 mg of *cis,cis,cis*-cyclonona-1,3,5-triene (**7**) in >90% purity by VPC: UV_{max} (EtOH) 296 nm (ϵ 1000); IR 2985, 1724, 1624, 1449, 1256, 670 cm^{-1} ; NMR δ 1.1 (m, 2), 2.4 (m, 4), 4.8–5.9 (m, 6, including a singlet, $W_{1/2} = 4$ Hz at 5.56). These data are in excellent agreement with published values.⁵

A small sample of triene **7** was dissolved in CCl_4 and the solution sealed into an NMR tube. The solution was heated for 2 h at 50 °C and *cis* diene^{2,5} was formed (NMR analysis).

Irradiation of *trans*-Bicyclo[4.4.0]deca-2,4-diene (5) at Room Temperature (254 nm). A Vycor tube containing 4 mL of a 4×10^{-2} M pentane solution of diene **5** and *n*-decane (5×10^{-3} M, internal standard) was purged with nitrogen (1.5 min), sealed with a serum stopper, and irradiated in the Rayonet reactor at 254 nm at 25–30 °C. The course of the reaction was analyzed by VPC and it was found that a single product was produced initially; upon continued irradiation (up to 7 h) two secondary products appeared. At the end of the reaction all starting material had been consumed, and the relative areas of the three product peaks were 5.4 to 1.4 to 1.

The UV spectrum of the reaction mixture in ethanol underwent a gradual loss of the original maximum at 262 nm and an increase in optical density in the 220–230-nm region. At the end of the experiment, only end absorption was evident above 220 nm.

Preparative Low-Temperature Irradiation of *trans*-Bicyclo[4.4.0]deca-2,4-diene (5). To an irradiation vessel consisting of a quartz immersion well fitted with a low-pressure mercury resonance lamp (254 nm) which was surrounded by a cooling jacket in which was circulated dry ice-chilled methanol was added a solution of 583 mg of diene **5** in 85 mL of pentane. The solution was agitated by a slow purge of pentane-saturated nitrogen and irradiated at 254 nm for 4.5 h (temperature of the outer wall of the cooling jacket was –63 °C), during which time VPC analysis

indicated that ca. 50% of the starting material was converted to a single major product plus one trace peak. The reaction mixture was stored in the dark for 11 h and irradiation was resumed for a further 7 h. The solvent was removed under mild vacuum at 25–30 °C and the residue was separated on a 12% AgNO_3 /silica gel dry column.⁶ In addition to starting material (diene **5**), the major component of the mixture was *cis*-bicyclo[4.4.0]deca-2,4-diene (**8**); also present were at least three trace compounds, one of which was identified as 2-*endo*,7-*endo*-tricyclo[5.3.0.0^{2,10}]deca-8-ene by its NMR spectrum.² The 2-*exo*,7-*endo* isomer was not detected. The identity of these two materials was established by comparison with authentic samples.²

Low-Temperature Reduction of Photoproducts of *trans*-Bicyclo[4.4.0]deca-2,4-diene (5). A solution of 20 mg (0.15 mmol) of *trans*-bicyclo[4.4.0]deca-2,4-diene in 4 mL of pentane was irradiated at –78 °C in the Rayonet reactor for 2.5 h and stored at –78 °C while a diimide reduction paste was prepared.¹⁰ A suspension of 2.0 g (10.3 mmol) of potassium diazodicarboxylate in a mixture of 4 mL of water and 3 mL of methanol was chilled to –78 °C. In a separate flask 1.25 g (20.6 mmol) of glacial acetic acid in 4 mL of methanol was chilled to –78 °C. A few drops of the acid solution was added to the rapidly stirred diazodicarboxylate slurry and 2 min later the cold photoproduct mixture was rapidly added, followed immediately by the remainder of the acetic acid solution. The mixture was allowed to warm gradually with stirring to room temperature overnight and was extracted with pentane. The organic extract was analyzed by VPC and showed more than five components present, one of which had a retention time identical with cyclodecane (by coinjection). The mixture was concentrated and hydrogenated over 10% Pd on charcoal at room temperature for several hours. The hydrogenated mixture was analyzed by VPC and was found to be less complex. On both polar and nonpolar VPC columns, the second largest peak had a retention time identical (coinjection) with that of authentic cyclodecane.

Irradiation of *trans*-Bicyclo[4.4.0]deca-2,4-diene (5) at 77 K in Methylcyclohexane Glass. To a high-vacuum manifold equipped with a 1-L mixing bulb was attached a flask containing 98 mg of diene **5**. After the diene was degassed via several freeze (77 K)–pump (2 μm)–thaw cycles, the mixing bulb was allowed to fill with diene vapor until a thermal-conductivity gauge attached to the system indicated 25–30 μm (uncorrected). The mixing bulb was sealed off and the remainder of the manifold was evacuated. The diene sample was replaced by a sample of spectral-grade methylcyclohexane (degassed) and the manifold, including the mixing bulb, was filled with methylcyclohexane vapor to an indicated 180 μm (uncorrected thermal-conductivity gauge). After being mixed, the contents of the mixing bulb were allowed to bleed into a liquid nitrogen cooled Air Products Dewar cell, where the vapor was condensed on a Suprasil quartz plate. The UV spectra of the resulting glass were recorded on a Perkin-Elmer 202 spectrometer equipped with a sample-chamber door modified to accept the Dewar cell. After an initial spectrum was recorded, the sample was irradiated at 254 nm (low-pressure resonance lamp) for 85 min. In contrast to the room-temperature solution spectrum, the initial spectrum of diene **5** at 77 K exhibited sharp maxima, with evident fine structure: UV_{max} (absorbance) 263 nm (0.45), 268 (0.29), 270 (0.51). The absorbance decreased sharply for $\lambda \geq 272$ nm and was near zero at 300 nm.

Upon irradiation, the overall UV optical density appeared to increase, and several new maxima at longer wavelength appeared after 10 min of irradiation and increased steadily throughout the irradiation. After 85 min of irradiation the following UV spectrum was obtained: UV_{max} (absorbance) 262 nm (1.06), 266 (0.90), 269 (1.26), 282 (0.84), (sh, 0.45), 310 (0.08).

Wavelength Effect on Photostationary State in the Irradiation of *trans*-Bicyclo[4.4.0]deca-2,4-diene (5). A quartz-tipped 4-mL irradiation vessel containing a solution of diene **5** (2.9×10^{-2} M) and *n*-decane (4.9×10^{-3} M, an internal standard) was cooled to –80 to –73 °C by a stream of cold N_2 gas and was irradiated at 254 nm in the Rayonet reactor for 1.5 h. The reaction mixture was analyzed by VPC and it was found that the ratio of diene **5** to triene **10** (analyzed as its thermal isomerization product, *cis* diene **8**) was 0.5 to 1. The solution was kept cold (–80 °C) as the Rayonet lamps were exchanged for RPR-3000-A lamps (maximum output near 300 nm), and irradiation

was continued at 300 nm. The solution was analyzed by VPC and it was found that concentration of triene **10** decreased and the concentration of diene **5** increased. The diene **5**-triene **10** ratio stabilized at 5:1 after 30 min and remained unchanged after a further 30 min of irradiation. The amounts of several trace-level products, which appeared during the initial 254-nm irradiation, did not appear to change during the 300-nm irradiation.

Irradiation of Argon Matrix Isolated *trans*-Bicyclo[4.4.0]deca-2,4-diene (5). A mixture of *trans*-bicyclo[4.4.0]deca-2,4-diene (**5**) (VPC purified and freeze-thaw degassed) and argon was prepared (diene pressure 1.4 torr, argon pressure 420 torr, diene 5:Ar = 1:300) and deposited on a sodium chloride plate cooled to 15–18 K by a CTI "Cryodyne" Model 20 refrigerator. A total of 6.42 mmol of the mixture was deposited at a rate of 1.7 to 2.5 mmol/h. The IR spectrum of the sample was recorded on a Perkin-Elmer PE-137 spectrometer, and the sample was irradiated via a Suprasil window, with a modified Mineralight UVS-1 254-nm lamp (the visible-light blocking filter had been removed), placed 8 cm from the sample. After irradiation, several new bands were observed in the IR spectrum at 1437 (weak sh), 990 (w), 954 (m), 862 (w), 841 (m, sh), and 758 (m) cm^{-1} . A decrease in the intensity of starting material bands at 883 cm^{-1} and 1470 cm^{-1} implied that $25 \pm 10\%$ of starting material had been consumed. The spectrum changed only slightly during further irradiation for a total of 18.75 h at 254 nm.

The 254-nm lamp was replaced with a 300-nm lamp, and irradiation was continued for 4.5 h. The intensity of the new bands decreased relative to those of starting material, but the deterioration of the quality of the matrix due to a slow air leak prevented the quantification of the changes.

Room-Temperature Irradiation of *trans*-Bicyclo[5.4.0]undeca-8,10-diene (6). A 4-mL Vycor tube containing 2 mL of a pentane solution of *trans*-bicyclo[5.4.0]undeca-8,10-diene (**6**) (4.8×10^{-2} M) and dodecane (6.7 mg) as an internal standard was purged with nitrogen, sealed, and irradiated in the Rayonet reactor at 254 nm and room temperature, over a period of 8.5 h. The course of the reaction was followed by VPC and the analysis indicated a rapid disappearance of starting material and the formation of two new products. After prolonged irradiation a third product was seen to develop. Material balance was very poor; starting material was consumed much faster than products were formed.

Low-Temperature Irradiation of *trans*-Bicyclo[5.4.0]undeca-8,10-diene (6). A Vycor tube containing 50 mL of a 4.5

$\times 10^{-2}$ M solution of diene **6** in pentane was placed in a quartz Dewar flask, cooled to -55°C with a stream of cold nitrogen gas, and irradiated at 254 nm for 4 h. The reaction mixture was analyzed by VPC and showed only a single major peak, with the retention time of the starting material, and one trace peak. However, analysis of the mixture by NMR and IR revealed the presence of *cis*-bicyclo[5.4.0]undeca-8,10-diene (IR absorbances at 730 and 674 cm^{-1} ; NMR δ 2.50, bridgehead protons) as well. After a further 2 h of irradiation, analysis by UV gave a spectrum similar to that of starting material. Irradiation was continued for a total of 12.5 h, during which time VPC analysis showed only one major peak, corresponding to the *cis* and *trans* dienes **12** and **6**, and one minor peak of shorter retention time than that of the dienes. The minor peak reached 5% of the reaction mixture after 12.5 h. The cold reaction mixture was concentrated under vacuum (-78°C) and reduced with diimide (prepared¹⁰ from 24.1 g (0.12 mol) of potassium diazodecarboxylate. The UV spectrum of the diimide reduction product mixture contained a broad, flat absorbance from 220 to 265 nm, indicating residual unsaturation. Therefore, the mixture was further reduced with H_2 over 10% Pd/carbon. The hydrogenated product mixture exhibited only end absorption above 200 nm. The two major components of the product mixture were isolated by preparative VPC. The component of shorter retention time was identified as bicyclo[5.4.0]undecane on the basis of the following spectral data: IR (neat) 2880 (s), 2830 (s), 1453 (m), 1439 (m), 954 (w) cm^{-1} ; NMR δ 0.7–1.9 (br m, maxima at 1.0 and 1.5); low-resolution mass spectrum (70 eV), m/e 153 (4.7), 152 (38), 67 (100); high-resolution mass spectrum, parent ion 152.1573, calcd for $\text{C}_{11}\text{H}_{20}$ 152.1565.

The component of longer retention time was identified as cycloundecane on the basis of the following spectral data: IR (neat) 2865 (s), 2801 (s), 1460 (m), 1431 (m), 746 (w) cm^{-1} ; NMR δ 1.42 (s, $W_{1/2} = 2$ Hz); low-resolution mass spectrum, m/e 155 (1.0%), 153 (9), 41 (100); high-resolution mass spectrum, parent ion 154.1714, calcd for $\text{C}_{11}\text{H}_{22}$ 154.1721.

Registry No. 4, 2144-23-2; 5, 7360-96-5; 6, 40095-24-7; 7, 1689-67-4; 8, 13304-05-7; 9, 40815-18-7; 10, 74063-32-4; 12, 40146-40-5; *cis*-bicyclo[4.3.0]nona-2,4-diene, 3054-91-9; 2,3-dibromo-*trans*-decalin, 16781-96-7; cycloheptanone, 502-42-1; butadiene, 106-99-0; bicyclo[5.4.0]undec-9-en-2-one, 74063-33-5; *cis*-bicyclo[5.4.0]undec-9-ene, 16613-71-1; *trans*-bicyclo[5.4.0]undec-9-ene, 21394-36-5; 9,10-dibromo-*trans*-bicyclo[5.4.0]undecane, 74063-34-6; bicyclo[5.4.0]undecane, 4443-69-0; cycloundecane, 294-41-7.

Chloroacetamide Photocyclization. Synthesis of 20-Deethylcatharanthine¹

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20-Deethylcatharanthine, a potential precursor of vinblastine-type dimeric indole alkaloids, has been synthesized in ten steps from 1-benzenesulfonylindole. The synthesis features a Diels-Alder reaction between 1-carbethoxy-1,2-dihydropyridine and ethyl 2-(1-benzenesulfonylindol-2-yl)acrylate to construct the 7-carbomethoxy-7-(2-indolyl)isoquinuclidine skeleton and photocyclization of an *N*-chloroacetyl derivative to introduce the C(5)-C(6) (tryptamine) bridge. Reduction of the lactam is achieved via the thiolactam. With the isolation of six intermediates, the overall yield is 5% from 1-benzenesulfonylindole.

The discovery² of the fragmentative coupling of catharanthine *N*-oxide with vindoline has opened for the first time a viable route to derivatives of the vinblastine series

of diindole alkaloids. Earlier routes^{3,4} had made available only systems of unnatural stereochemistry at C-16'. Much subsequent activity has centered on applying this method

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