acetates **7**,[16] and silyl enol ethers **5**. Since alkynolate anion formation occurs with complete retention of starting ester stereochemistry,[1] the derived reduction products are also formed with retained stereochemistry; thus, the endo ester **24a** affords only endo products **25a**, **26a**, and **27a**, while exo ester **24b** affords only exo products. The extended scope of products afforded by the remarkable reduction reaction reported herein, coupled with the stereochemical integrity of the original homologation chemistry, combine to provide a broad new methodology which should be useful in organic synthesis.

Supplementary Material Available: Spectroscopic and analytical data for **10–12**, **14**, **18**, (*E*)- and (*Z*)-**22**, **23**, **25a**,**b**, **26a**, **27a**,**b**, **28b**, **29a**,**b**, **30**, and **31** (3 pages). Ordering information is given on any masthead page.

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[16] For references to the general preparation of enol esters, see: Mitsudo, T.; Yoshihisa, Y. H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1566.

Synthesis of Eight-Membered Carbocycles via Intramolecular [6π + 2π] Photocycloaddition of Alkenyltropones

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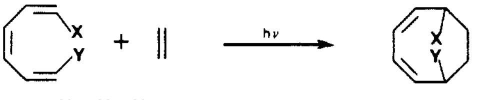
The synthesis of carbocyclic natural products containing a bicyclo[6.3.0]undecane skeleton has been of considerable interest recently.[1] Approaches to the preparation of the cyclooctane portion of these structures have utilized acyclic closure,[1k] fragmentation,[1f,g] and ring expansion[1c–e] strategies. Herein, we report the direct construction of the bicyclo[6.3.0]undecane nucleus via a novel [6π + 2π] intramolecular photochemical cycloaddition reaction.[2f]

A straightforward symmetry "allowed" photochemical cycloaddition of a linearly conjugated 6π-electron system with a 2π-electron moiety (eq 1) would certainly fall victim to alternative

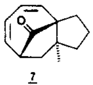
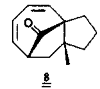
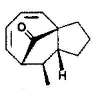
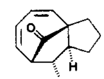
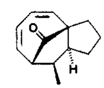
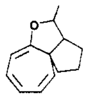
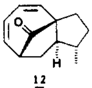
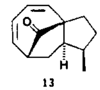
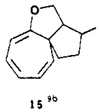


(1)

1a X = Y = H **2a**
1b X,Y = CO **2b**

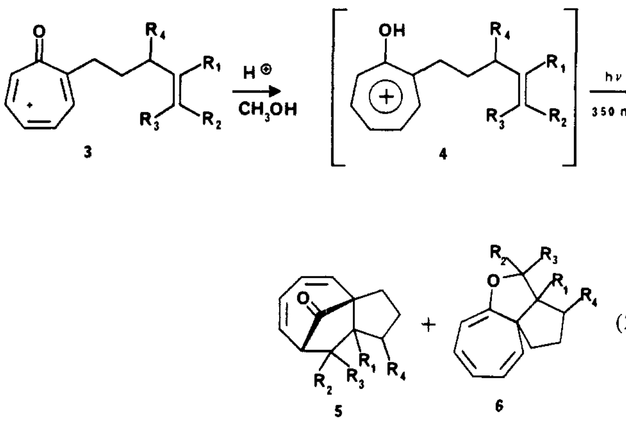
modes of reaction, such as electrocyclization of the triene or [2π + 2π] cycloaddition.[2] One 6π-electron system in which these undesired reaction pathways are minimized is tropone (**1b**).[3,4] Tropone and its derivatives have a rich photochemical history, although [6π + 2π] cycloaddition with a simple alkene has not been reported.[3–5]

Table I

alkenyl tropone 3[9a]	Cycloadducts[9b,c]			
3a: $R_1 = CH_3$		 **7** 18(5)	 **8** 48(20)	
3b: $R_2 = CH_3$	 **9** 10(5)	 **10** 37(18)	 **11** 5	 **14**[9a] 31(15)
3c: $R_3 = CH_3$		43(22)	8(5)	31(14)
3d: $R_4 = CH_3$		 **12** 28(19)	 **13** 13(4)	 **15**[9b] 29(14)

We recognized that a successful [6π + 2π] cycloaddition reaction would depend critically on the alkene intercepting an excited state of tropone in the desired regiochemical orientation prior to the intervention of other unwanted photochemical processes.[3,4] An intramolecular variant of this tropone/alkene cycloaddition strategy seemed a reasonable way to provide sufficient kinetic and regiochemical advantages to allow this reaction to occur.

In fact, when we irradiated alkenyltropone **3** in various aprotic solvents complex reaction mixtures resulted from which only minor amounts of cycloadducts were isolated. However, upon irradiation in *acidic* methanol, the desired intramolecular [6π + 2π] cycloaddition reaction proceeded smoothly to produce adduct **5** along with lesser amounts of the isomeric [8 + 2] adduct **6**[5] (eq 2). The requirement for acid implicates the *hydroxytropylium ion* **4** as the 6π-electron component in this cycloaddition and represents one of the novel features of this process.



(2)

In a typical experiment, a 20 mM solution of alkenyltropone **3**[6] in 4:1 methanol/1 M H_2SO_4 was irradiated at room temper-

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[1] (a) Boeckman, R. K., Jr.; Bershas, J. P.; Clardy, J.; Solheim, B. *J. Org. Chem.* **1977**, *42*, 3630. (b) Das, T. K.; Dutta, P. C. *Synth. Commun.* **1976**, *6*, 253. (c) Paquette, L. A.; Andrews, D. R.; Colapret, J. A. *J. Org. Chem.* **1985**, *50*, 201. (d) Gadwood, R. C.; Lett, R. M.; Wissinger, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 3869. (e) Danheiser, R. L.; Gee, S. K.; Sard, H. *J. Am. Chem. Soc.* **1982**, *104*, 7670. (f) Coates, R. M.; Senter, P. D.; Baker, W. R. *J. Org. Chem.* **1982**, *47*, 3597. (g) Dauben, W. G.; Hart, D. J. *J. Org. Chem.* **1977**, *42*, 922. (h) Pattenden, G.; Teague, S. J. *Tetrahedron Lett.* **1984**, 3021. (i) Mehta, G.; Murty, N. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1058. (j) Grayson, D. W., Wilson, J. R. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1695. (k) Takeshita, H.; Kato, N.; Nakanishi, K.; Tagoshi, H.; Hatsui, T. *Chem. Lett.* **1984**, 1495. (l) Gadwood, R. C. *J. Chem. Soc., Chem. Commun.* **1985**, 123.

[2] (a) Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry" Academic Press: West Berlin, 1970. (b) Mori, A.; Takeshita, H. *Chem. Lett.* **1975**, 599. (c) Bellus, D.; Helferich, G.; Weis, C. D. *Helv. Chim. Acta* **1971**, *54*, 463. (d) See also ref 3f. (e) Yang, N. C.; Chiang, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 3163. (f) Houk has recently reported the thermal intramolecular [6π + 2π] cycloaddition of *cross-conjugated trienes* with enamines to yield triquinanes. Houk, K. N.; Wu, T.-C. *J. Am. Chem. Soc.* **1985**, *107*, 5308.

[3] (a) Mukai, T.; Tsuruta, H.; Takeshita, A.; Watanabe, H. *Tetrahedron Lett.* **1968**, 4065. (b) Tezuka, T.; Akasaki, Y.; Mukai, T. *Tetrahedron Lett.* **1967**, 1397. (c) Kende, A. S.; Lancaster, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 5283. (d) Tezuka, T.; Akasaki, Y.; Mukai, T. *Tetrahedron Lett.* **1967**, 5003. (e) Mukai, T.; Tezuka, T.; Akasaki, Y. *J. Am. Chem. Soc.* **1966**, *88*, 5025. (f) Kende, A. S. *J. Am. Chem. Soc.* **1966**, *88*, 5026.

[4] (a) For example, see: Kobayashi, T.; Hirai, T.; Tsunetsugo, J.; Hayashi, H.; Nozoe, T., *Tetrahedron* **1975**, *31*, 1483 and references cited therein. (b) van Tamelen, E. E.; Greeley, R. H.; Schumacher, H. *J. Am. Chem. Soc.* **1971**, *93*, 6151.

[5] Intermolecular [8 + 2] photoaddition of alkenes to tropone has been described: Cantrell, T. S. *Tetrahedron Lett.* **1975**, 907 and references cited therein.

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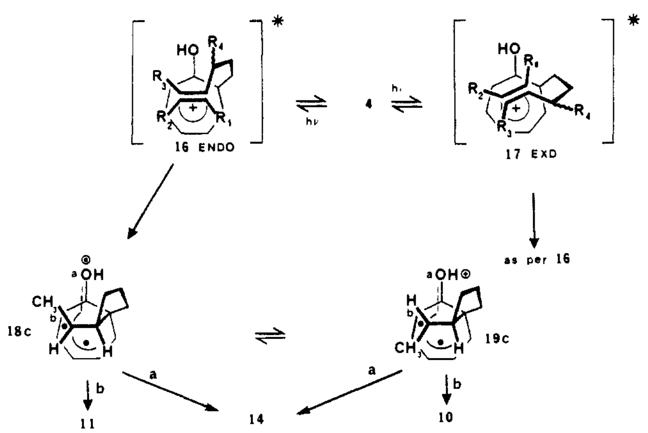
Scheme I



ature with 350-nm light. When GLC analysis indicated consumption of starting material (30–60 min), the cycloadducts were isolated by chromatography on silica gel. Representative results are shown in Table I.

Examination of the cycloadduct structures reveals the regiochemical and stereochemical complexity of this reaction. The regiochemistry of addition (i.e., [6 + 2] vs. [8 + 2]) is sensitive to the location of the methyl substituent on the alkenyl side chain, as exclusive [6 + 2] cyclization results only when $R_1 = CH_3$ (**3a**).

When the stereochemical outcome of the [6π + 2π] cyclization of alkenyl tropones **3a–c** is considered, two issues must be addressed: (1) the endo vs. exo mode of cycloaddition and (2) the loss of alkene stereochemistry upon [6 + 2] cyclization of **3b** and **3c**. Quite surprisingly, the exo mode of addition, which produces the highly strained *trans*-bicyclo[3.3.0]octane adduct **8**,[10] is favored upon irradiation of **3a**. Furthermore, irradiation of either the (*E*)-alkenyl tropone **3b** or the *Z* isomer **3c** resulted in product distributions containing virtually identical ratios of endo [6 + 2] adducts **10** and **11** to [8 + 2] adduct **14**. Control experiments demonstrated that the (*E*)- and (*Z*)-alkenyl tropones do not interconvert under the reaction conditions, indicating that alkene stereochemistry is not lost prior to cycloaddition.

To account for the regiochemical and stereochemical results of this unique tropylium–alkene photocyclization reaction, we suggest a mechanism shown in Scheme I. Our hypothesis features stereochemical control through initial exciplex formation, followed by regiochemical control through eventual diradical collapse with either carbon–carbon or carbon–oxygen bond formation.

We postulate that the ratio of endo (**7**, **10–13**) to exo (**8**, **9**) products of [6π + 2π] cycloaddition reflects the relative populations, and hence stabilities, of the diastereomeric parallel plane exciplexes **16** and **17** formed upon electronic excitation of hydroxytropylium precursor **4**. It is plausible that placing a methyl substituent directly over the cationic ring disrupts the stabilizing solvation by the nucleophilic solvent and raises the energy of that exciplex.[11] Thus, irradiation of **4a** and **4c** would generate exciplexes **16a** and **17c** which both experience this destabilizing interaction. Therefore, the major products of these cycloadditions are derived from the alternative exciplexes **17a** and **16c**, respectively.

For simplicity, the remainder of the scheme is detailed for the endo tropylium exciplex **16c** derived from (*Z*)-alkenyltropone **3c**. Collapse of this endo exciplex would produce diradical **18c** which can lose initial alkene stereochemistry through equilibration with the diastereomeric diradical **19c**. According to our mechanistic hypothesis, the strain inherent in the *trans*-bicyclo[3.3.0]octane portion of adducts **8** and **9** is not imparted until the final bond closure step. The step that determines stereochemistry (collapse of exciplexes **17a** or **17b** with carbon–carbon bond formation) occurs prior to introduction of this strain, and therefore the product stereochemistry is simply a consequence of exciplex stability.

In summary, we have developed an efficient synthesis of functionalized bicyclo[6.3.0]undecane carbocycles through an intramolecular [6π + 2π] photocycloaddition reaction of alkenyltropones. The regiochemical and stereochemical outcome of this reaction can be rationalized through a novel mechanistic pathway. Applications of this [6π + 2π] photocyclization reaction to the synthesis of cyclooctane-containing natural products are in progress.

Acknowledgment. We thank the Syntex-Russell Marker Fund and a Schering-Plough Corporation Grant of Research Corporation of financial support and Dr. M. Parvez for performing the X-ray crystallography analysis of **8**.

Supplementary Material Available: Tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and labeled diagrams for **8** (6 pages). Ordering information is given on any current masthead page.

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[6] The alkenyltropones used in this study were prepared by addition of the corresponding alkenyl Grignard reagents to 2-chlorotropone: **3a**, 80%; **3b**, 26%; **3c**, 42%; **3d**, 30%. Doering, W. v. E.; Hiskey, C. F. *J. Am. Chem. Soc.* **1952**, *74*, 5688.

[7] (a) Rn = H unless otherwise noted. (b) The yields in Table I are reported as GLC yield (isolated yield) percent. Sensitivity of the cycloadducts to chromatographic purification typically resulted in diminished recovered yields.

[8] All new compounds exhibited satisfactory spectral data (^1H NMR, ^{13}C NMR, IR, MS, high-resolution MS, UV). The stereochemistry of the cycloadducts could be deduced from an examination of extensive ^1H NMR decoupling and difference NOE data. The complete structure and stereochemistry of cycloadduct **8** was determined by single-crystal X-ray analysis. Crystal data for **8**: $C_{13}H_{16}O$; M 188.3; monoclinic; space group $P2_1/n$; a = 13.038 (4) Å, b = 6.437 (1) Å c = 13.004 (3) Å, β = 105.53 (2)°; V = 1051.6 Å^3; Z = 4; D_{calcd} = 1.19 g cm^{-3}; Enraf-Nonius CAD4 diffractometer, MO $K\alpha$ (λ = 0.71073 Å) radiation, μ = 0.68 cm^{-1}; 864 observed reflections [$I > 3\sigma(I)$] refined to a conventional R = 0.072 (R_w = 0.079).

[9] Identical 1:1 mixture of two stereoisomeric [8 + 2] adducts were isolated from irradiation of either **3b** or **3c**. The stereochemical assignments for these isomers is still being investigated. (b) A 1:1 mixture of stereoisomeric [8 + 2] adducts was recovered from irradiation of **3d**. These adducts were not further characterized.

[10] Molecular mechanics calculations suggest that exo adduct **8** is ca 9 kcal/mol less stable than endo adduct **7**.

[11] A similar arguement can be invoked to rationalize the stereochemical outcome of the Diels–Alder cycloaddition between tropylium tetrafluoroborate and cyclopentadiene in water. See: Ito, S.; Itoh, I. *Tetrahedron Lett.* **1971**, 2969. Clemans, G. B.; Dobbins, M. A. *Tetrahedron Lett.* **1982**, 382.

Synthesis of Polyoxygenated Hydrocarbons via Radical-Mediated Oxygenation of Vinylcyclopropanes

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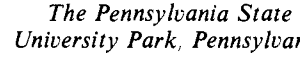
Received September 9, 1985

The development of regio- and stereocontrolled methods for introduction of oxygen into unsaturated hydrocarbons has led to the construction of many complex polyoxygenated natural products. For example, recent advances in the epoxidation or hydroxylation of alkenes afford a general solution to the synthesis of the vicinal diol segments common to many antibiotics and carbohydrates.[1] The corresponding oxidation of cyclopropanes (eq 1) has received scant attention,[2] despite its potential for direct



(1)

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† Author to whom inquiries regarding the X-ray data should be addressed.

[1] (a) Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron Lett.* **1983**, 3943. (b) Christ, W. J.; Cha, J. K.; Kishi, Y. *Ibid.* **1983**, 3947. (c) Behrens, C. W.; Sharpless, K. B. *Aldrichimica Acta* **1983**, *16*, 67 and references cited therein.

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