hexane at −78 °C as a white solid and characterized by spectroscopy and analysis as the benzene C–H activation product *trans*-Cp*Re(CO)(PMe_3)(H)(Ph) (**4**). By way of comparison, we observed (Figure 1c,d) that irradiation of Cp*Re$(CO)_2(PMe_3)$[5] under identical conditions gave only a low yield of **4**. The assignment of mutually trans H and C_6H_5 groups in **4** is based on the following results. The $^2J_{PH}$ value for the hydride resonance (66.7 Hz) indicates cis hydride and PMe_3 groups; the CO resonance has J_{CH} = 10.8 Hz and no observable coupling to P, indicating CO to be cis to the hydride and trans to PMe_3.[7] Furthermore, a strong NOE enhancement of the hydride and phenyl resonances resulted from irradiation of the PMe_3 proton signal. Additional confirmation comes from a comparison with the NMR spectra of the new compounds *cis*- and *trans*-Cp*Re(CO)(PMe_3)Br_2 (**5**) and *trans*(H,Br)-Cp*Re(CO)(PMe_3)(H)(Br) (**6**) that have been synthesized in thermal reactions of **1**. The CO resonance in *cis*-**5** is coupled to the cis phosphorus atom with $^2J_{PC}$ = 24.9 Hz, whereas the CO resonance in *trans*-**5** is coupled to the trans phosphorus atom by only 3.7 Hz. Likewise, **6** is assigned a structure with trans CO and PMe_3 groups because $^2J_{PC}$ is too small to observe in the CO resonance, and it also has *cis*-PMe_3 and hydride groups from the value of $^2J_{PH}$ (55.7 Hz) for the hydride resonance (and the observation of a very strong NOE enhancement of this resonance on irradiating the PMe_3 protons).

Photolysis of **1** in hexane or cyclohexane for 10 min resulted in the complete disappearance of the dinitrogen complex and the formation of a single carbonyl product with a very strong, sharp ν(CO) at 1878 cm^{-1}. This was isolated at −78 °C as a white solid and characterized as the cyclometalated compound Cp*Re(CO)(η^2-PMe_2CH_2)(H) (**7**) resulting from intramolecular C–H activation of a methyl group of the PMe_3 ligand. The stereochemistry, in which the hydride is trans to the methylene carbon and cis to P, is assigned from NMR couplings and NOE results. The latter allows an unambiguous assignment of the inequivalent PMe and CH resonances. Compound **7** reacts slowly with benzene in the dark to form the hydridophenyl **4**. This suggests that reversible formation of "Cp*Re(CO)PMe_3" from **7** occurs[5] and that **4** results from the thermal reaction of this intermediate with benzene. Consistent with this, when benzene-d_6 was employed the hydride resonance was totally absent in the NMR spectrum, proving that the product is exclusively Cp*Re(CO)(PMe_3)(D)(C_6D_5) and that the hydride of **7** is reincorporated wholly into the PMe_3 group of **4**, with the hydride of **4** arising wholly from the benzene solvent.

The reversible formation of "Cp*Re(CO)(PMe_3)" from **7** is further indicated by the quantitative regeneration of the dinitrogen complex **1** when **7** is pressurized with N_2. More surprising is the observation that **1** is also formed essentially quantitatively (but more slowly) in hexane from the hydridophenyl complex **4** and N_2. This may indicate that, in solution **4** is partly dissociated into benzene and "Cp*Re(CO)(PMe_3)" possibly via a benzene π-complex intermediate.[8] In agreement, the NMR and MS of **4** indicated about 20% conversion to Cp*Re(CO)(PMe_3)(D)(C_6D_5) in C_6D_6 at 8 °C over 6 days.

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Supplementary Material Available: Synthetic, spectral, and analytical data for compounds **1** and **3–7** (4 pages). Ordering information is given on any current masthead page.

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[7] For related stereochemical dependence of J_{PC} and J_{PH} in cis and trans piano stool carbonyl phosphine compounds, see: (a) Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151. (b) Pyshnograyeva, N. I.; Setkina, V. N.; Panosyan, G. A.; Petrovskii, P. V.; Makarov, Yu. V.; Kolobova, N. E.; Kursanov, D. N. *Ibid.* **1976**, *108*, 85. (c) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

[8] Benzene complexes of Cp*Re$(CO)_3$ have recently been identified: Van der Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576.

Charge-Transfer Sensitization of the Valence Photoisomerization of Norbornadiene to Quadricyclene by an Orthometalated Transition-Metal Complex

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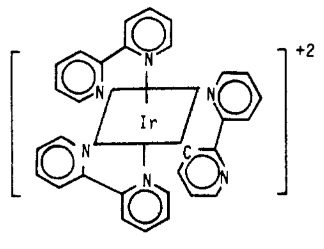
Some time ago we reported[1] that the orthometalated complex (2,2′-bipyrid-3-yl-C^3,N')bis(2,2′-bipyridine-N,N')iridium(III) (**1**)



1

sensitizes the valence photoisomerization of norbornadiene (**2**) to quadricyclene (**3**) with high quantum efficiency (eq 1). This

(1)

2, R = H
4, R = CO_2CH_3

3, R = H
5, R = CO_2CH_3

result was surprising on energetic grounds in that the lowest electronic excited state of **1** lies well below the reactive triplet state of the diene. Consequently, we have undertaken a more detailed investigation of the **1–2** system with the aim of delineating the key sensitizer–substrate interaction(s). Presented here are several lines of evidence that support a novel mechanism based upon photoinduced charge transfer.

Excitation of **1**[2] with 366-nm light produces a green luminescence[3] (λ_{max} 462, 491 nm) having a lifetime of 10.2 μs[4] in freshly purified acetonitrile at 25 °C. Addition of **2** strongly quenches this emission with no discernible alteration in band shape. Lifetime quenching data obey Stern–Volmer kinetics and yield a value of 1.4×10^8 M^{-1} s^{-1} for k_q, the bimolecular quenching rate constant. The quantum efficiency (ϕ_{isom}) for sensitized isomerization of **2** to **3** upon 366-nm irradiation in N_2-bubbled CH_3CN at 25 °C varies with both the diene concentration and the length of photolysis.[5] Measurements of ϕ_{isom} at short irradiation times were used to construct a linear plot of $1/\phi_{isom}$ vs. 1/[**2**], from which values of 1.4×10^8 M^{-1} s^{-1} for k_q and 0.72 ± 0.05 for the limiting sensitization efficiency were obtained. The excellent agreement between the quenching rate constants calculated from lifetime and photochemical data argues strongly that the emissive excited state of **1** sensitizes the valence isomerization of **2**.

The photobehavior of the **1–2** system can be analyzed in terms of the general mechanism outlined in eq 2, where an asterisk

$$\begin{aligned} \mathbf{1}^* + \mathbf{2} \rightleftarrows [\mathbf{1}^*,\mathbf{2}] &\xrightarrow{\text{i}} \mathbf{1} + {}^3\mathbf{2} \rightarrow \mathbf{1} + \mathbf{2} \text{ or } \mathbf{1} + \mathbf{3} \\ &\xrightarrow{\text{ii}} \text{X} \rightarrow \mathbf{1} + \mathbf{2} \text{ or } \mathbf{1} + \mathbf{3} \qquad (2) \end{aligned}$$

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[1] Kutal, C. *Adv. Chem. Ser.* **1978**, *168*, 158.

[2] Synthesis: Kahl, J. L.; Hanck, K.; DeArmond, K. *J. Inorg. Nucl. Chem.* **1979**, *41*, 495.

[3] (a) This luminescence originates from an excited state containing contributions from intraligand and metal-to-ligand charge-transfer configurations.[3b–d] (b) Watts, R. J.; Harrington, J. S.; Van Houten, J. *J. Am. Chem. Soc.* **1977**, *99*, 2179. (c) Braterman, P. S.; Heath, G. A.; MacKenzie, A. J.; Noble, B. C.; Peacock, R. D.; Yellowlees, L. J. *Inorg. Chem.* **1984**, *23*, 3425. (d) Finlayson, M. F.; Ford, P. C.; Watts, R. J. *J. Phys. Chem.*, in press.

[4] Because of self-quenching, the luminescent lifetime of **1** varies with concentration. Lifetime values measured in CH_3CN at 25 °C are as follows: 10.2 μs (1×10^{-6} M), 10.2 μs (1×10^{-5} M), 0.1 μs (4×10^{-4} M).

[5] Competitive quenching by **3** (vide infra) formed photochemically lowers ϕ_{isom} at longer irradiation times.

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Table I. Summary of Rate Constants for Luminescence Quenching of **1** and Half-Wave Oxidation Potentials of Quenchers

quencher	k_q, M^{-1} s^{-1} [a]	$E_{1/2}^{ox}$, V vs. SCE[b]
3	3.3×10^9	0.91
2	1.4×10^8	1.56
5	1.0×10^7	1.64
4	$<1 \times 10^5$	2.06

[a] Measured in CH_3CN at 25 °C; [**1**] = 7.8×10^{-6} M. Samples were degassed by five freeze-pump-thaw cycles. [b] Values taken from ref 11.

denotes an electronically excited state. Diffusion together of **1*** and **2** produces an encounter complex which can partition between two pathways: (i) formation of the triplet state of **2** via collisional (exchange) energy transfer or (ii) formation of a charge-transfer stabilized complex X. Subsequent relaxation processes of the diene triplet and X lead to the ground states of **1** and either **2** or **3**.

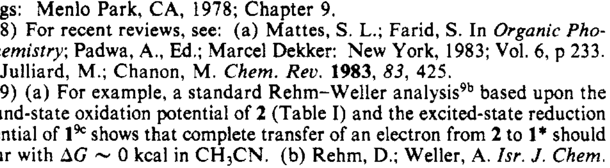
Sensitization via electronic energy transfer (eq 2, path i) from the emissive state of **1** (E = 62 kcal[3b]) to the lowest vertical triplet state in **2** (E = 70 kcal[6]) would be highly endothermic. The rate constant (k_{et}) for this activated process can be estimated by use of eq 3,[7] where k_{dif} is the rate constant for diffusional encounter

$$\log\left(\frac{k_{dif}}{k_{et}}\right) = \frac{\Delta E}{2.3RT} \qquad (3)$$

and ΔE is the donor-acceptor state energy difference. Setting $k_{dif} = 1 \times 10^{10}$ M^{-1} s^{-1} [7] and ΔE = 8 kcal yields $k_{et} = 1 \times 10^4$ M^{-1} s^{-1} at 25 °C. Since this value is 10^4 times smaller than the experimentally measured quenching constant, we can exclude classical energy transfer from **1*** to the vertical triplet of **2** as a significant pathway for sensitization.

Numerous quencher-quenchee pairs for which energy transfer would be appreciably endothermic have been shown to interact via complete or partial transfer of an electron (eq 2, path ii).[8] In the present case, energetic considerations suggest that **1*** should function as an electron acceptor toward **2**.[9] Evidence to support this type of process comes from a study of the quenching of **1*** by a series of norbornadienes and quadricyclenes having a range of oxidation potentials (Table I). The inverse correlation between k_q and $E_{1/2}^{ox}$ is clearly consistent with a quenching mechanism involving some degree of electron transfer from the organic substrate to **1***.[10]

Photoinduced electron transfer also provides an attractive explanation for the sensitized isomerization of **2**. Thus a net transfer of electron density from **2** to **1*** within the charge-transfer complex X weakens the bonding between carbon atom pairs C_1–C_2 and C_3–C_4 while enhancing that between C_1–C_4 and C_2–C_3 (eq 4).[12]



(4)

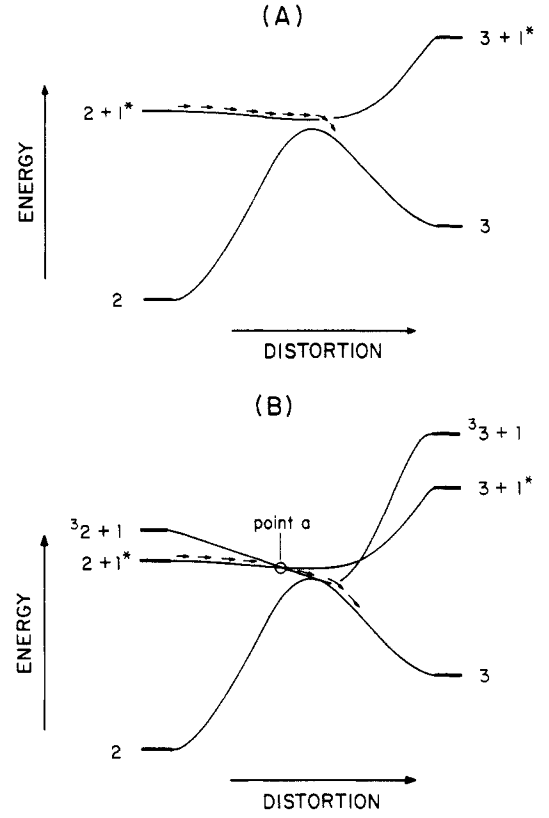


Figure 1. Possible pathways for the **1**-sensitized photoisomerization of **2** to **3**. (A) Potential energy surface for the charge-transfer-stabilized complex (X) between **1*** and **2** funnels directly to the ground-state structure of **3**. (B) Crossing (point a) occurs from the surface representing X to the triplet surface connecting **2** and **3**; once populated, the triplet relaxes to **3** with high efficiency.

These changes in bond order generate a polarized and structurally distorted organic substrate[6] which is favorably disposed toward rearrangement to **3**. Figure 1A illustrates this pathway in terms of postulated potential energy surfaces; thus relaxation from the minimum in the surface representing X to the ground state leads to efficient formation of **3**. Alternatively, Figure 1B depicts the situation in which the system initially moves along the X surface until, at some critical geometry (point a), crossing to the diene triplet surface occurs.[13] Most importantly, this surface switch produces a distorted diene triplet whose energy is well below that of the vertical triplet state of **2**.[14]

While additional studies are needed to decide which of the above reaction trajectories (Figure 1A,B) provides the more accurate description of the sensitization process, it should be emphasized that both paths evolve from *partial* electron transfer between **1*** and **2**. Complete transfer of an electron (e.g., eq 5) can be

$$\mathbf{1}^* + \mathbf{2} \rightarrow X \rightarrow Ir(bpy\text{-}N,N')_2(bpy\text{-}C,N')^+ + \mathbf{2}^{+\cdot} \qquad (5)$$

discounted on grounds that a fully developed norbornadiene radical cation ($\mathbf{2}^{+\cdot}$) is considerably more stable than its quadricyclene analogue ($\mathbf{3}^{+\cdot}$).[6b] Consequently, the rearrangement of $\mathbf{2}^{+\cdot}$ to $\mathbf{3}^{+\cdot}$ possesses too high an activation barrier to be of importance in any sensitization sequence. Energetics also militate against a mechanism involving recombination of a geminate ion pair (e.g., reverse of eq 5) to yield the vertical triplet state of **2**.[15] Such a process would be highly endothermic (~9 kcal) and thus of low proba-

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(6) For a discussion of energetics and structure in the **2**–**3** system, see: (a) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7388. (b) Raghavachari, K.; Haddon, R. C.; Roth, H. D. *Ibid.* **1983**, *105*, 3110.

(7) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 9.

(8) For recent reviews, see: (a) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233. (b) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425.

(9) (a) For example, a standard Rehm-Weller analysis[9b] based upon the ground-state oxidation potential of **2** (Table I) and the excited-state reduction potential of **1**[9c] shows that complete transfer of an electron from **2** to **1*** should occur with $\Delta G \sim 0$ kcal in CH_3CN. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (c) Bergeron, S. F.; Watts, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 3151.

(10) Similarly, **3** quenches the luminescence of **1** (4.3×10^{-4} M, Cl^- counterion) 45 times more rapidly than **2** in a 1:9 (vol/vol) methanol-benzene solution.

(11) Gassman, P. G.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

(12) (a) Hoffman, R. *Acc. Chem. Res.* **1971**, *4*, 1. (b) Schwendiman, D. P.; Kutal, C. *Inorg. Chem.* **1977**, *16*, 719.

(13) For a related example of excited-state curve crossing, see: Jones, G., II; Becker, W. G.; Chiang, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 1269.

(14) Generation of a distorted triplet state following photoinduced electron transfer has been reported for the isomeric 1,2-diphenylcyclopropanes. Wong, P. C.; Arnold, D. R. *Tetrahedron Lett.* **1979**, *23*, 2101.

(15) For an example where the ion recombination-triplet pathway results in efficient isomerization of a substituted norbornadiene, see: Schwarz, W.; Dangel, K.-M.; Jones, G., II; Bargon, J. *J. Am. Chem. Soc.* **1982**, *104*, 5686.

bility. Consistent with the view that full electron transfer does not play a significant role in the mechanism of sensitization, we find no evidence for the formation of Ir(bpy-N,N')$_2$(bpy-C,N')$^+$ upon flash photolysis of **1** and **2** in CH_3CN.[16]

Acknowledgment. We thank Dr. Guillermo Ferraudi of the Notre Dame Radiation Laboratory for performing exploratory flash photolysis experiments. Financial support from the National Science Foundation (Grant CHE-8210558) is gratefully acknowledged.

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(16) The electronic absorption spectrum of the reduced iridium complex has been reported.[3c] Also see: Cohen, H.; Slama-Schwok, A.; Rabani, J.; Watts, R. J.; Meyerstein, D. *J. Phys. Chem.* **1985**, *89*, 2465.

Synthesis of (−)-Bertyadionol

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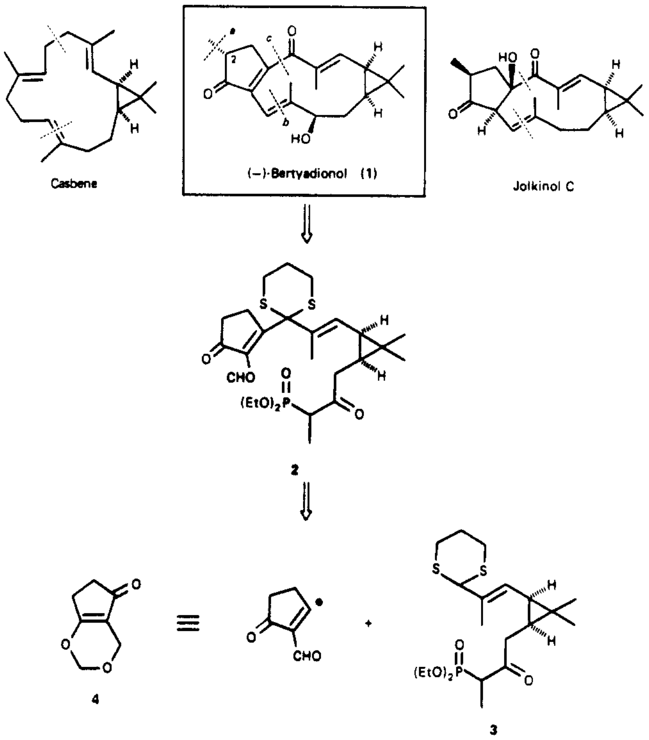
We disclose here a unified strategy that recently culminated in a total synthesis of (−)-bertyadionol (**1**), the first member of the lathyrane diterpenes to succumb to synthesis.[3] Our interest in this class[4] stems from the close structural relationship to the pharmacologically important *Crotonoideae* subfamily,[5] members of which display proinflammatory and tumor-promoting activity.[6]

Bertyadionol (**1**) was isolated by Jefferies from *Bertya cupressoidea* (*Euphorbiaceae*), a plant endemic to Western Australia. A preliminary report including a tentative structure appeared in 1970.[7] Several years later the relative and absolute stereochemistries were secured through a combination of degradation and double-resonance NMR experiments.[8] Of considerable importance from the synthetic perspective was the reported instability of bertyadionol toward mild acid, base, and ultraviolet light, as well as to both nucleophiles and electrophiles.[7,8]

Our approach, applicable to other macrocyclic diterpenes within the casbene–lathryane class, called for union of **3**, derived from (−)-*cis*-chrysanthemic acid, with an appropriately functionalized cyclopentenyl synthon.[9] For bertyadionol (**1**), vinylogous ester **4**[10] (a vinyl cation equivalent) appeared ideal.[11] Intramolecular keto phosphonate cyclization generating the requisite *E* configuration at C(5,6) would then provide the macrocyclic ring.[12,13] Finally, introduction of the stereocenters at C(2) and C(7) was envisioned to take advantage of the inherent stereochemical bias of the macrocyclic skeleton.[14]



Casbene

(−)-Bertyadionol (1)

Jolkinol C

2

4

3

With this as background, preparation of **3** began with (−)-*cis*-chrysanthemic acid (**5**, 88–92% ee).[15] Arndt–Eistert homologation[16] followed by regioselective allylic oxidation [SeO_2, pyr][17] and then careful[18] dithioacetal formation [propylene dithiol,

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(1) Camille and Henry Dreyfus Teacher-Scholar, 1978–1983; National Institutes of Health (National Cancer Institute) Career Development Awardee, 1980–1985; J. S. Guggenheim Fellow, 1985–1986.

(2) American Cancer Society Postdoctoral Fellow, 1983–1985.

(3) The total synthesis of (−)-bertyadionol was first announced at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985; paper ORGN 27.

(4) Other members of the lathyrane family include the jolkinols (Ghisalbert, E. L.; Jefferies, P. R.; Toia, R. F.; Worth, G. K. *Tetrahedron* **1974**, *30*, 3269) and diterpene D (Uemera, D.; Nobuhara, K.; Nakayama, Y.; Shizuri, Y.; Hirata, Y. *Tetrahedron Lett.* **1976**, 4593).

(5) For a comprehensive review, see: Evans, F. J.; Taylor, S. E. *Progress in the Chemistry of Organic Natural Products*; Springer-Verlag: Wien, New York, 1983; Vol. 44, pp 2–99.

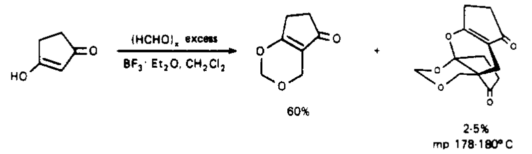
(6) Schmidt, R. J.; Evans, F. J. *Arch. Toxicol.* **1980**, *44*, 279. Kupchan, S. M.; Uchida, I.; Branfman, A. R.; Dailey, R. G.; Yefei, B. *Science* (*Washington, D.C.*) **1976**, *191*, 571.

(7) Ghisalberti, E. L.; Jefferies, P. R.; Payne, T. G.; Worth, G. K. *Tetrahedron Lett.* **1970**, 4599.

(8) Ghisalberti, E. L.; Jefferies, P. R.; Payne, T. G.; Worth, G. K. *Tetrahedron* **1973**, *29*, 403.

(9) To test the feasibility of this unified strategy, we initially completed a total synthesis of (−)-casbene employing the TBS-ether of 6-chloro-4-methyl-4-hexen-1-ol and **3**; unpublished results of M. S. Malamas and T. Maeda.

(10) Although unknown, vinylogous ester **4** was prepared in analogy to several closely related derivatives as illustrated below; see: Bolte, M. L.; Crow, W. D.; Yoshida, S. *Aust. J. Chem.* **1982**, *35*, 1411. The structure of the propellane was secured via X-ray analysis.[25]



(11) For examples of 1,2-additions of dithianes to a vinylogous esters, see: Quesada, M. L.; Schlessinger, R. H. *Synth. Commun.* **1976**, *6*, 555. Tobin, P. S.; Basu, S. K.; Gosserode, R. S.; Wheeler, D. M. S. *J. Org. Chem.* **1980**, *45*, 1250.

(12) Dauben, W. G.; Robbins, J. D. *Tetrahedron Lett.* **1975**, 151 and references cited therein. Lang, M.; Prasad, K.; Holick, W.; Gosteli, J.; Ernest, I.; Woodward, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 6296. Ernest, I.; Gosteli, J.; Woodward, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 6301. Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 5699. Aristoff, P. A. *Synth. Commun.* **1983**, *13*, 145.

(13) (a) Burri, K. F.; Cardone, R. A.; Chen, W. Y.; Rosen, P. *J. Am. Chem. Soc.* **1978**, *100*, 7069. (b) Stork, G.; Nakamura, E. *J. Org. Chem.* **1979**, *44*, 4010. (c) Nicolaou, K. C.; Seitz, S. P.; Pavia, M. R.; Petasis, N. A. *J. Org. Chem.* **1979**, *44*, 4011. (d) Nicolaou, K. C.; Seitz, S. P.; Pavia, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 2030.

(14) (a) Still, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 2493. (b) Vedejs, E.; Dolphin, J. M.; Mastalerz, H. *J. Am. Chem. Soc.* **1983**, *105*, 127 and references cited therein.

(15) Resolution of (±)-chrysanthemic acid was achieved by preparation of the (−)-*N*-methylephedrin salt and then fractional recrystallization (hexanes).

(16) Horner, L.; Spietschka, E. *Chem. Ber.* **1952**, *85*, 225. For a review, see: Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32.

(17) Camps, F.; Coll, J.; Parente, A. *Synthesis* **1978**, 215.

(18) If dithioacetal formation is attempted at temperatures >−23 °C, a Lewis acid promoted rearrangement takes place.

0002-7863/86/1508-3110$01.50/0