the published procedure[7] by using a 1 M solution of thallic trifluoroacetate in trifluoroacetic acid [1–1.2 equiv of $Tl(O_2CCF_3)_3$]. The procedure was modified for aryl alcohols with one or more activating groups on the ring by diluting the solution with 5 mL of tetrahydrofuran and stirring overnight at room temperature. The solvents were then removed under vacuum and the arylthallium intermediates carbonylated without further purification. Palladium chloride (0.1 mmol), anhydrous lithium chloride (2 mmol), magnesium oxide (2 mmol), and 5 mL of methanol were placed in a round-bottomed flask with a septum inlet. The system was flushed with carbon monoxide and the arylthallium compound dissolved in 5 mL of methanol was added, after which the system was again flushed with carbon monoxide and maintained under a 1 atm pressure. After the reaction had stirred overnight at room temperature, the product was isolated by standard extractive and recrystallization procedures, or the yield was determined by gas chromatography using an internal standard.

This thallation–carbonylation procedure has proven to be quite general for a variety of other aromatic compounds as well. Thus, thallation–carbonylation of benzoic and phenylacetic acids yields phthalic and homophthalic anhydrides, respectively (entries 9 and 10), and benzamide affords phthalimide in excellent yield (entry 11). In a similar fashion, acetanilide[17] is cyclocarbonylated to acetylanthranil (entry 12). The versatility of this procedure should prove useful in the synthesis of a large variety of interesting heterocyclic systems. At present we are examining further applications of these ortho-thallated intermediates in organic synthesis.

Acknowledgment. We gratefully acknowledge the generous financial support of the National Institutes of Health and also Matthey Bishop Inc. and Engelhard Industries for supplying the palladium chloride.

Registry No. Benzene, 71-43-2; methyl benzoate, 93-58-3; *tert*-butylbenzene, 98-06-6; methyl *tert*-butylbenzoate, 26537-19-9; benzenemethanol, 100-51-6; 1(3*H*)-isobenzofuranone, 87-41-2; 3-methoxybenzenemethanol, 6971-51-3; 5-methoxy-1(3*H*)-isobenzofuranone, 4741-62-2; 3-hydroxybenzenemethanol, 620-24-6; 5-hydroxy-1(3*H*)-isobenzofuranone, 55104-35-3; benzeneethanol, 60-12-8; 3,4-dihydro-1*H*-2-benzopyran-1-one, 4702-34-5; *cis*-2-phenylcyclohexanol, 16201-63-1; *cis*-1,2,3,4,4a,10b-hexahydro-6*H*-dibenzo[*b*,*d*]pyran-6-one, 72331-10-3; *trans*-2-phenylcyclohexanol, 2362-61-0; *trans*-1,2,3,4,4a,10b-hexahydro-6*H*-dibenzo[*b*,*d*]pyran-6-one, 72331-11-4; thallic trifluoroacetate, 23586-53-0.

(17) For a recent report on the direct palladation of acetanilide, see: Horino, H.; Inoue, N. *Tetrahedron Lett.* **1979**, 2403–6.

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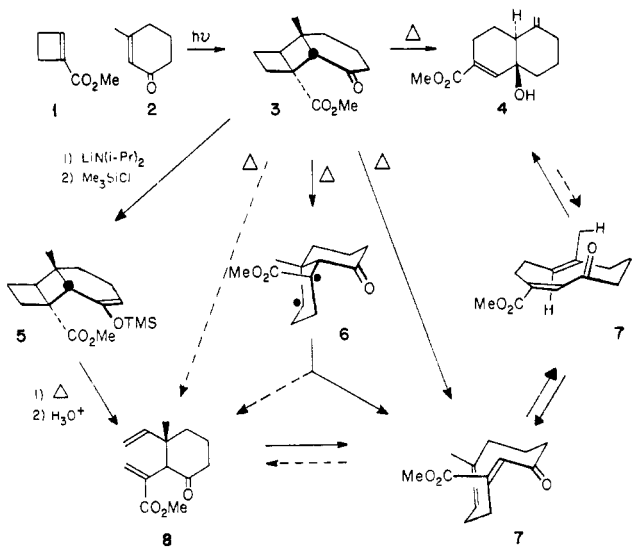
Olefin Metathesis–Transannular Ene Sequence. A Method for the Stereocontrolled Synthesis of *trans*-Decalin Derivatives. 1. Total Synthesis of (±)-Calameon[1]

Summary: The salient mechanistic and synthetic features of a method for the stereocontrolled synthesis of *trans*-decalin derivatives based on the thermolysis of photoadducts derived from methyl cyclobutenecarboxylate and 3-alkylcyclohex-2-enones are presented.

Scheme I



Sir: Synthetic approaches to various steroids, alkaloids, and terpenes draw heavily on methodology for the synthesis of *trans*-decalin derivatives. The most commonly used approaches to these derivatives include the reduction of octalones derived from Robinson annelations, epimerization of *cis*-decalin derivatives prepared from Diels–Alder cycloadditions, polyene cyclizations, and Michael additions to enones followed by enolate trapping.[2] These strategies which involve the elaboration of a latent ring-junction bond are topologically differentiated from an approach in which the ring-junction bond and stereochemistry are simultaneously established through transannular closure of a medium-ring precursor.[3] While the synthetic potential of this approach can be appreciated from a consideration of its role in the biosynthesis of various *trans*-decalin natural products[4] and of studies on transannular reactions,[5] its use in synthesis is limited by the paucity of methodology for the facile preparation of suitably functionalized medium-ring intermediates. We describe herein a method for the synthesis of *trans*-decalin derivatives based on the closure of cyclodecadienones easily derived from readily available precursors by a photothermal olefin metathesis sequence.[6]

(1) Presented in part at the ACS/CSJ Chemical Congress, Honolulu, Hawaii, Apr 1–6, 1979, No. ORGN 115.

(2) For representative applications of these strategies in terpene synthesis, see: Heathcock, C. H. "The Total Synthesis of Natural Products"; ApSimon, J., Ed.; Wiley: New York, 1973; Vol. 2, pp 197–558.

(3) For an analysis of design considerations pertinent to the synthesis of polycyclic structures, see: Corey, E. J.; Howe, W. J.; Orf, H. W.; Pensak, D. A.; Petersson, G. *J. Am. Chem. Soc.* **1975**, *97*, 6116.

(4) See, for example: Cordell, G. A. *Chem. Rev.* **1976**, *76*, 425.

(5) For studies pertinent to the work presented herein, see: (a) Terada, Y.; Yamamura, S. *Tetrahedron Lett.* **1979**, 1623. Niwa, M.; Iguchi, M.; Yamamura, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3148. (b) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476. (c) Scovell, E. G.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1978**, 529.

(6) Recently, independent studies on (a) the pyrolysis of the piperitone photoadduct **13** (Lange, G. L.; McCarthy, F. C. *Tetrahedron Lett.* **1978**, 4749) and (b) the pyrolysis of the photoadduct (i) derived from methylcyclobutene and piperitone (Williams, J. R.; Callahan, J. F. *J. Chem. Soc., Chem. Commun.* **1979**, 404, 405) have been reported. The product stereochemistry presented in the former study differs from that expected on the basis of the mechanistic analysis and the supporting calameon synthesis presented herein (cf. ref 5a, 6b, and 8, and references cited therein). With respect to synthetic utility, it is notable that the photoadducts derived from ester **1** are converted to *trans*-decalin derivatives in significantly higher yields than the corresponding photoadducts derived from (i). Our studies on this point suggest that relative to the methyl group the ester subunit may serve to facilitate the cycloreversion reaction, activate the ketone carbonyl for the ene reaction, and stabilize the product (cf. ref 18).

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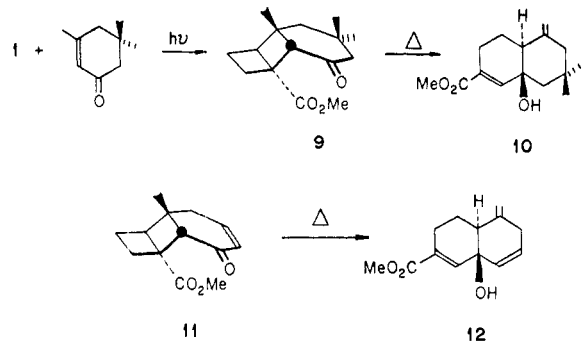
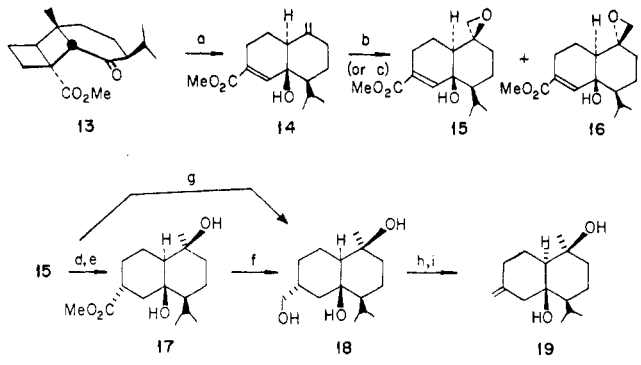
Scheme II



Scheme III



[a] 200 °C, C_6H_6, 5 h. [b] *m*-$ClC_6H_4CO_3H$, CH_2Cl_2. [c] $Mo(CO)_6$, *t*-BuOOH. [d] H_2, PtO_2, EtOH, NaOAc. [e] Epimer of 17 + NaOMe, MeOH. [f] $LiAlH_4$, Et_2O. [g] Li, NH_3, *t*-BuOH. [h] *o*-$NO_2C_6H_4SeCN$, $P(n\text{-}Bu)_3$. [i] H_2O_2, THF.

On the basis of our previous studies on a metathetical strategy for medium-ring synthesis,[7] thermolysis of photoadduct **3** would be expected to give cyclodecadienone **7** via a concerted cycloreversion process or an orbital-overlap-controlled fragmentation of a diyl intermediate (**6**) (Scheme I).[8] This sequence would serve, therefore, as a convenient route to cyclodecadienones which, under the conditions of their generation, could assume a conformation suitable for acid-catalyzed or thermal (ene) closure to trans-fused products (e.g., **3** → **7** → **4**).[5a] In accord with this analysis, photoadduct **3**[9] [prepared in 78% yield based on **1** by irradiation (Pyrex filter) of the enone and **1** in methylene chloride solution maintained at ca. −78 °C] when heated at 206 °C for 2.5 h in toluene (resealable Pyrex tube) provided ester **4** (92%, mp 91.5–92.5 °C).[10] The intermediacy of cyclodecadienone **7** in this transformation is suggested by its formation from partial pyrolysis (190 °C, 7 min, $PhCH_3$) of photoadduct **3** and its independent and efficient conversion at 206 °C (15 min, $PhCH_3$) to ester **4**. Ester **8**, which may also be derived from cycloreversion of **3**, was not detected in the thermolysis of **3** or **7**. However, it was found that pyrolysis (206 °C, 15 min, $PhCH_3$) of ester **8** (independently prepared from **3** by the indicated sequence) also gave the trans-fused product **4** (ca. 90% yield) by initial Cope rearrangement to **7**. Thus, the trans-fused product **4** obtained in this case may arise from either product of the cycloreversion process.

In further studies, we have found that this two-step method is general for a variety of 4-, 5-, or 6-substituted 3-alkylcyclohex-2-enones. For example, pyrolysis of the isophorone photoadduct **9** gave ester **10** (mp 93–94 °C)[11] in 96% yield (Scheme II). As such, this reorganization is not prevented by the development of substantial 1,3-diaxial interactions in the formation of intermediates or product. The method can also be extended to unsaturated systems (e.g., **11** → **12**,[12] 39% yield). The lower yield obtained in the formation of **12** is presumably a reflection of the increased strain associated with the closure reaction and/or the relative instability of the bis allylic, tertiary alcohol product.

For monosubstituted systems, such as photoadduct **13**,[13] a particularly important mechanistic and synthetic feature arises in that two trans-fused products may be obtained. If cyclodecadienone conformational equilibration is rapid, the ratio of these products would be a reflection of the orientation preference (equatorial vs. axial) of the substituent in the closure transition state (kinetic control) or product (thermodynamic control). In accord with either circumstance, thermolysis of the piperitone photoadduct **13** gave ester **14** (97% yield)[14] in which the isopropyl substituent is equatorially oriented as demonstrated by the following conversion of **14** to (±)-calameon (**19**)[6] (Scheme III). Thus, treatment of ester **14** with *m*-chloroperbenzoic acid gave epoxides **15** (68% yield) and **16** (23% yield). Greater stereoselectivity (>95%) for this epoxidation was obtained at the expense of low conversions (ca. 30%) by using molybdenum hexacarboxyl/*tert*-butylhydroperoxide.[15] Hydrogenation of epoxide **15** afforded a mixture of ester epimers from which ester **17** was obtained in an overall yield of 77% after epimerization of the axial ester isomer. Reduction of **17** afforded triol **18** (96% yield, mp 142.5–143.5 °C), which was also obtained in one

(7) Wender, P. A.; Lechleiter, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 267.

(8) (a) For discussions pertinent to the mechanism of such cycloreversions, see: Paquette, L. A.; Schwartz, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 3215. Goldstein, M.; Benzon, M. S. *Ibid.* **1972**, *94*, 5119, 7147. Komornicki, A.; McIver, J. W. *Ibid.* **1976**, *98*, 4553. Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Wade, L. E. *Ibid.* **1977**, *99*, 5069. Gajewski, J. J.; Conrad, N. D. *Ibid.* **1978**, *100*, 6268. (b) Cycloreversion of **3** involving a concerted process or orbital-overlap-controlled fragmentation of a diyl intermediate would be expected (cf. ref 8a) to provide **7**, the *E,E* product, rather than the other allowed isomer of **7**, the *Z,Z* product, due to unfavorable ester–ring interactions which arise in the transition state leading to the latter. Spectroscopic support for the *E,E* stereochemistry is found in a comparison of the NMR, IR, and UV data of **7** [NMR ($CDCl_3$) δ 7.17 (s, 1 H); IR (CH_2Cl_2) 1715, 1685 cm^{-1}; UV (cyclohexane) 228 nm] and the *E* isomer of methyl 2-methyl-4-oxopent-2-enoate, the parent system [NMR ($CDCl_3$) δ 7.07; IR (CCl_4) 1725, 1695 cm^{-1}; UV (95% EtOH) 235 nm (cf. El-Ghandour, N.; Henri-Rousseau, O.; Soulier, J. *Bull. Soc. Chim. Fr.* **1972**, 2817)], and related compounds. The λ_{max} of 228 nm for **7** would be expected to shift toward 235 nm in 95% EtOH, a solvent system which was not used for this determination due to the instability of **7**.

(9) Satisfactory spectroscopic data and elemental or exact mass analyses were obtained for all new compounds.

(10) **4**: IR (CH_2Cl_2) 3550, 1710, 1640 cm^{-1}; UV (95% EtOH) 225 nm (ε 3300); NMR ($CDCl_3$) δ 1.62 (s, 1 H), 1.4–2.8 (m, 11 H), 3.75 (s, 3 H), 4.69 (br s, 1 H), 4.94 (br s, 1 H), 6.76 (t, 1 H, $J \approx 3$ Hz).

(11) **10**: IR (CH_2Cl_2) 3570, 1710, 1655 cm^{-1}; UV (95% EtOH) 223 nm (ε 4800); NMR ($CDCl_3$) δ 0.99 (s, 3 H), 1.07 (s, 3 H), 1.43 (s, 1 H), 1.30–2.80 (m, 9 H), 3.73 (s, 3 H), 4.74 (br s, 1 H), 4.92 (br s, 1 H), 6.76 (t, 1 H, $J \approx 2$ Hz).

(12) **11** was prepared by conversion of **3** to the corresponding trimethylsilyl enol ether (LDA followed by Me_3SiCl) which was then treated with $Pd(OAc)_2$. **12**: IR (CH_2Cl_2) 3560, 1720, 1655 cm^{-1}; UV (95% EtOH) 230 nm (ε 5500); NMR ($CDCl_3$) δ 1.44 (s, 1 H, exchanges with D_2O), 1.5–2.85 (m, 5 H), 2.93 (br s, 2 H), 3.76 (s, 3 H), 4.87 (br s, 1 H), 5.05 (br s, 1 H), 5.92 (br s, 2 H), 6.90 (t, 1 H, $J \approx 2$ Hz).

(13) Prepared from the irradiation of piperitone in the presence of ester **1** (62% yield based on **1**, 95% yield based on piperitone). Cf.: Wender, P. A.; Lechleiter, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4321 and ref 6a.

(14) **14**: IR (neat) 3510, 1720, 1650 cm^{-1}; UV (95% EtOH) 223 nm (ε 4400); NMR ($CDCl_3$) δ 0.96 (d, 6 H, $J = 7$ Hz), 1.42 (s, 1 H, exchanges with D_2O), 1.25–2.75 (m, 11 H), 3.76 (s, 3 H), 4.68 (br s, 1 H), 4.95 (br s, 1 H), 7.22 (br s, 1 H) (cf. ref 6a).

(15) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136. Baker, T. N.; Mains, G. J.; Sheng, M. N.; Zajacek, J. G. *J. Org. Chem.* **1973**, *38*, 1145.

step (21% yield) by lithium–ammonia reduction of epoxide **15**. Finally, triol **18** was converted to (±)-calameon (**19**, 81% yield)[16] according to the method reported by Grieco, Gilman, and Nishizawa.[17]

It is a noteworthy consequence of the reagents, solvent, and reaction conditions used in this method for *trans*-decalin synthesis that the conversion of starting materials to product may be conducted without isolation of intermediates. Moreover, since the photolysis and thermolysis can be conducted at high reactant concentration (e.g., ca. 0.5–2.0 M), preparative-scale reactions are easily performed. Further studies on this method and its extension[18] are in progress.

Acknowledgment. This investigation was supported by Grant No. CA21136, awarded by the National Cancer Institute, DHEW. We thank Professor S. Yamamura for samples of calameon and isocalamenediol.

(16) The IR and NMR spectroscopic data and chromatographic properties of synthetic calameon were identical in all respects with authentic material kindly provided by Professor S. Yamamura.
(17) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485.
(18) Wender, P. A.; Letendre, L. J. *J. Org. Chem.*, following paper in this issue.
(19) Fellow of the Alfred P. Sloan Foundation, 1979–1981.

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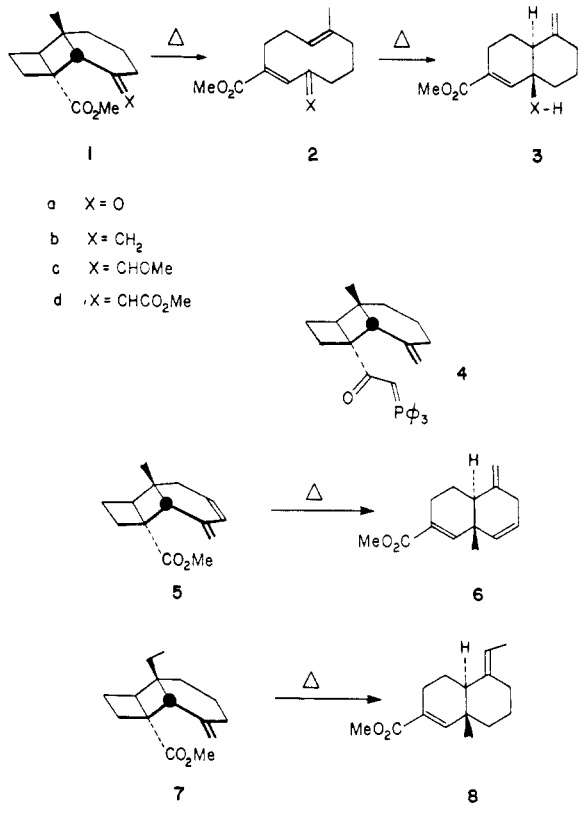
Olefin Metathesis–Transannular Ene Sequence. A Method for the Stereocontrolled Synthesis of *trans*-Decalin Derivatives. 2. Formal Eudesmane Syntheses[1]

Summary: *trans*-Decalin derivatives with an alkyl substituent at the ring junction can be prepared by thermolysis of readily available derivatives of photoadducts derived from methyl cyclobutenecarboxylate and 3-alkylcyclohex-2-enones.

Sir: In the preceding communication, we presented the mechanistic and synthetic groundwork for a method for the conversion of readily available cycloalkenones to *trans*-decalin derivatives with a hydroxyl group at the ring junction (**1a** → **2a** → **3a**).[2] In view of the potential value of this concept in the synthesis of *trans*-decalin natural products characterized by a methyl or other alkyl group at the ring junction, we became interested in determining whether methylene analogues (e.g., **1b**) of the readily available photoadducts would undergo the efficient reorganization observed for the parent ketones.[2] The salient results of these studies are presented below.

Our attention was focussed initially on the suitability of this method for the preparation of derivatives with an angular methyl group (e.g., **3b**) due to the widespread occurrence of this structural element in various natural

Scheme I



products. However, the ketone-to-methylene transformation (**1a** → **1b**) required in this regard was found to be unexpectedly nontrivial. For example, reaction of photoadduct **1a**[2a] with methylenetriphenylphosphorane generated by treatment of methyltriphenylphosphonium bromide with *n*-butyllithium in THF or sodium hydride in Me_2SO produced the desired product **1b**[3,4] in reproducibly low yields (30–47%) along with varying amounts of **4**. Other olefination procedures provided no improvement in yield. However, it was eventually found that the formation of the undesired byproduct (**4**) in this Wittig methylenation could be eliminated when the ylide was generated with sodium *tert*-amylate and the olefination reaction conducted in toluene.[5] Under these conditions, methylene ester **1b** was formed in 88% yield. Commercially available potassium *tert*-amylate/cyclohexane was also found to be equally effective. It is conceivable that relative to Me_2SO the nonpolar solvent (toluene or cyclohexane) serves to inhibit the ion formation required in the penultimate step of the undesired ester-to-ylide transformation, leading to **4**.

The subsequent study on the thermal reorganization of the methylene ester **1b** was found to be less problematic. Thus, when this compound (**1b**) was heated at 210 °C for 2 h in toluene (resealable Pyrex tube), the *trans*-decalin derivative **3b**[6] was formed in 95% yield. The course of this reorganization is presumably analogous to that described for the rearrangement of **1a** to **3a**,[2a] and, as such, its efficiency is similarly decreased in the case of unsaturated systems (e.g., **5** → **6**; 245 °C, 6 h, 78% yield)[7] and relatively

(1) Presented in part at the ACS/CSJ Chemical Congress, Honolulu, Hawaii, Apr 1–6, 1979, No. ORGN 115.
(2) (a) Wender, P. A.; Hubbs, J. C. *J. Org. Chem.*, preceding paper in this issue. (b) For related independent studies, see: Lange, G. L.; McCarthy, F. C. *Tetrahedron Lett.* **1978**, 4749. Williams, J. R.; Callahan, J. R. *J. Chem. Soc., Chem. Commun.* **1979**, 404, 405.
(3) Satisfactory spectroscopic data and elemental and/or exact mass analyses were obtained for all new compounds.
(4) **1b**: IR (CCl_4) 2910, 1735, 1650 cm^{-1}; NMR ($CDCl_3$) δ 1.05 (s, 3 H), 1.1–2.8 (m, 11 H), 3.08 (s, 1 H), 3.61 (s, 3 H), 4.74 (d, 2 H).
(5) Conia, J.-M.; Limasset, J.-C. *Bull. Soc. Chim. Fr.* **1967**, 1936.
(6) **3b**: IR (film) 2910, 1730, 1650 cm^{-1}; NMR ($CDCl_3$) δ 0.84 (s, 3 H), 1.50–2.50 (m, 11 H), 3.73 (s, 3 H), 4.52 (m, 1 H), 4.80 (m, 1 H), 6.77 (t, 1 H, J = 1.9 Hz); UV (95% EtOH) 222 nm (ε 6500).

0022-3263/80/1945-0367$01.00/0