Photochemistry of Bichromophoric Molecules. Intramolecular Excited-State Interactions in the *cis*- and *trans*-Decalin-Connected Aryl Olefins: 7-Methylene-4bβ-methyl-4bβ,5,6,7,8,8aβ,9,10-octahydrophenanthrene[1] and Its 8aα Isomer

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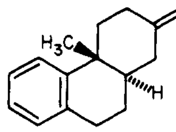
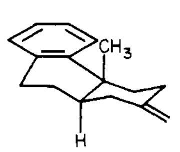
The photochemistry and photophysics of the title compounds (**1**, **2**) are reported. The *trans*-decalin **1** is relatively photoinert but the cis isomer (**2**) undergoes a singlet-derived, intramolecular, 1,3 photocycloaddition to give **13** (ϕ = 0.046). It is proposed that **13** is formed via an intramolecular exciplex (Scheme II) as in the acyclic analogue, 6-phenyl-2-hexene (**3**), with a rate constant for complexation, k_{ex}, equal to 5.4×10^6 s^{-1}. This is 185-fold slower than k_{ex} for **3** and corresponds to a ΔG_{298} (=8.2 kcal/mol) which can be equated with a requisite half-chair/chair to half-chair/boat isomerization (eq 3). Though neither **1** nor **2** is phosphorescent at 77 K, **2** sensitizes the isomerization of 1-methycyclohexene to methylenecyclohexane at room temperature in solution. Thus, intermolecular triplet-energy transfer is competitive with intramolecular energy transfer. Compound **13** efficiently (ϕ = 0.51) photocycloeliminates to give a carbene-derived product, **15**.

The photochemistry and photophysics of nonconjugated, bichromophoric molecules continue to be a subject of active interest,[1-3] with appreciable attention in recent years devoted to the excited-state properties of aryl olefins.[3-5] Irradiation of these latter compounds with 254-nm light gives rise to a number of intramolecular interactions involving the two functionalities, such as[4] (1) singlet exciplex formation, (2) singlet charge transfer, (3) enhanced triplet radiationless decay, (4) triplet energy transfer, and (5) di-π-methane bonding. The chemical consequences include such diverse reactions as olefin E/Z isomerization, anti-Markownikoff addition to the double bond, and olefin cycloaddition to the aromatic ring.[4]

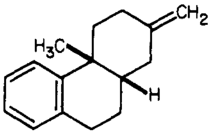
Our own studies have evolved from acyclics to polycyclics as we probe the dependence of these interactions on the spatial relationship of the chromophores. The tricyclic *trans*- and *cis*-decalins **1** and **2** fit naturally into this series, since the functional group separation (ca. 4.5 Å) in the rigid **1** (cf. **1a**) is greater than any we have yet explored, while the conformationally mobile **2** allows the functionalities to approach (in **2a**) the coplanar relationship available to 6-phenyl-2-hexene (**3**, cf. **3a**). We have proposed[4,6] that the rapid ($k = 1.0 \times 10^9$ s^{-1})[7] formation of conformer **3a** after excitation leads to the virtually quantitative production of a singlet exciplex which results in facile (ϕ = 0.26) intramolecular cycloaddition (eq 1) and extensive radiationless decay. This paper details some photochemical and spectroscopic properties of **1** and **2**; it also describes an unusual photocycloelimination of the photoproduct of **2**.[8]



1



1a



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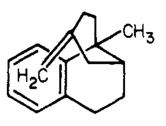
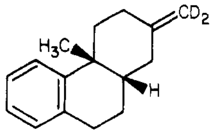
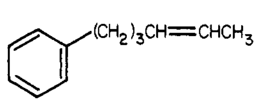


2a



2-d_2



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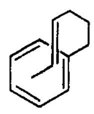
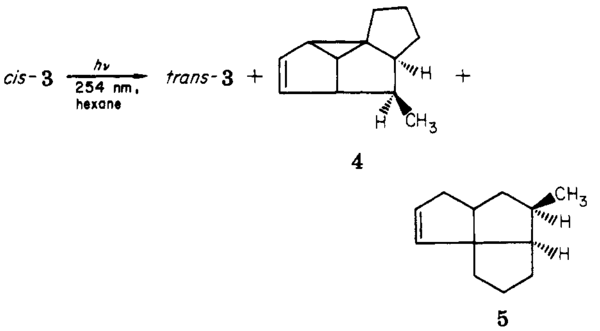


3a



(1)

Results

Preparation of 7-Methylene-4bβ-methyl-4bβ,5,6,7,8,8aα,9,10-octahydrophenanthrene (1). This compound was synthesized in a straightforward manner

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(1) (a) Organic Photochemistry. 45. Part 43: H. Morrison, *Acc. Chem. Res.*, **12**, 383 (1979). Part 44: H. Morrison and A. Miller, *J. Am. Chem. Soc.*, **102**, 372 (1980). (b) Abstracted from the Doctoral Dissertation of M.P., Purdue University, 1978.

(2) (a) For leading references, see F. Scully, T. Nylund, F. Palensky, and H. Morrison, *J. Am. Chem. Soc.*, **100**, 7352 (1978). (b) More recent examples include T. Hamada, Y. Okuno, M. Ohmori, T. Nishi, and O. Yonemitsu, *Heterocycles*, **8**, 251 (1977) (and earlier papers in this series); H. D. Becker and K. Sandros, *Chem. Phys. Lett.*, **55**, 498 (1978); J. A. Cairn, C. L. Braun, P. Caluwe, and M. Szwarc, *ibid.*, **54**, 469 (1978); J. A. Ors and R. Srinivasan, *J. Chem. Soc., Chem. Commun.*, 400 (1978); H. E. Zimmerman, M. G. Steinmetz, and C. L. Kreil, *J. Am. Chem. Soc.*, **100**, 4146 (1978); R. S. Givens and W. K. Chae, *ibid.*, **100**, 6278 (1978); M. J. Mirbach, A. Henne, and K. Schaffner, *ibid.*, **100**, 7127 (1978); K. Maruyama and Y. Kubo, *ibid.*, **100**, 7772 (1978). Bichromophores are finding utility as photostabilizers; cf. G. Irick, Jr., C. A. Kelly, and J. C. Martin, *Chem. Abstr.*, **90**, P39583a (1979) and (earlier patents in this series).

(3) A. Gilbert and G. N. Taylor, *J. Chem. Soc., Chem. Commun.*, 129 (1978); 229 (1979).

(4) Recently reviewed; cf. H. Morrison, *Org. Photochem.*, **4**, 143 (1979). See also ref 1a above.

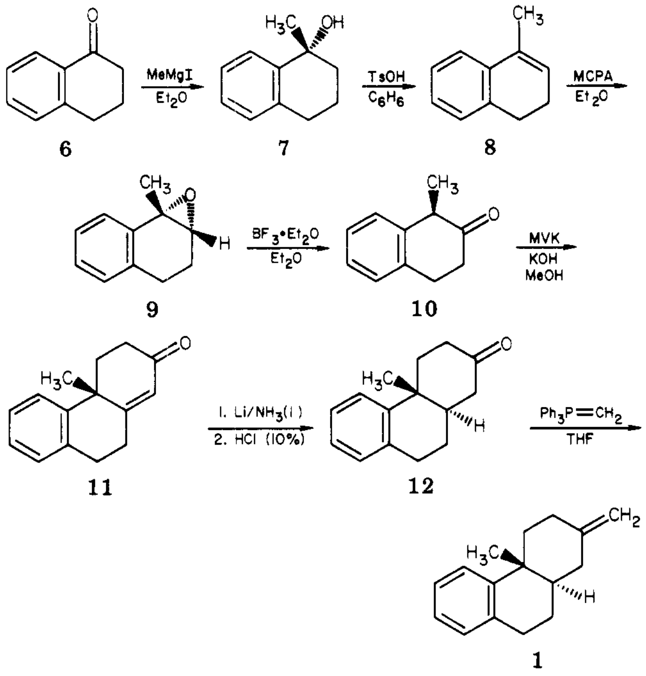
(5) T. Nylund and H. Morrison, *J. Am. Chem. Soc.*, **100**, 7364 (1978).

(6) H. Morrison and W. Ferree, Jr., *J. Chem. Soc. D*, 268 (1969); W. Ferree, Jr., J. Grutzner, and H. Morrison, *J. Am. Chem. Soc.*, **93**, 5502 (1971).

(7) Our most recent estimate, based on a measurement of $^1\tau$ for *cis*-**3** of 1.0 ns (D. Giacherio, unpublished results).

(8) Part of this work has been presented in preliminary form; cf. M. Pallmer and H. Morrison, *J. Chem. Soc., Chem. Commun.*, 558 (1978).

Scheme I

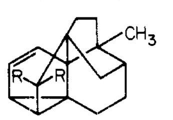


as outlined in Scheme I. The critical step is the metal/ammonia reduction of 11 which produces 12 in 65% yield.

Preparation of 7-Methylene-4bβ-methyl-4bβ,5,6,7,8,8aβ,9,10-octahydrophenanthrene (2). The *cis*-decalin was prepared in an analogous fashion with 10% Pd/C in methanol containing 2% acetic acid to reduce 11 to the cis isomer of 12.[9] The 9:1 mixture of *cis*- and *trans*-1 is formed in 72% yield and *cis*-12 is readily purified by VPC for Wittig olefination to 2 and 2-d_2.

Photolysis of 1. Irradiation of a 9.0 × 10^{-3} M solution of 1 in hexane for 1.25 h using 254-nm light (Rayonet) failed to produce any VPC-detectable products.

Photolysis of 2. Irradiation of a 0.02 M solution of 2 in hexane or *t*-butyl alcohol, using a low-pressure mercury arc, resulted in the formation of a single *primary* photoproduct detectable by VPC (a *secondary* photoproduct is also formed; see below). We assign the structure of this product as 13 (R = H) on the basis of the following evidence: the photoproduct is isomeric with 2, contains no aryl protons, and shows UV absorption ($\lambda_{\text{shoulder}}$ (hexane) 217 nm (ϵ 1350)) characteristic of a vinylcyclopropane.[6] Likewise, the product is readily hydrogenated to a saturated tetrahydro derivative, although ^{13}C NMR confirms the existence of only one double bond (signals at δ 130.39 (d) and 128.68 (d)).



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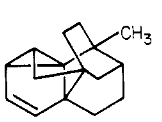

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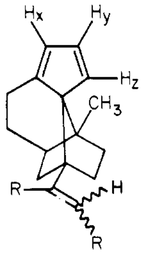
Intramolecular 1,3 cycloaddition[10] has therefore occurred,[11] with 12 structures possible (on paper! A number are impossibly strained.). Eight are inconsistent with the vinyl region of the ^{1}H NMR (δ 5.80–5.65 (1 H, dd, J = 2.0 and 5.5 Hz) and 5.60–5.45 (1 H, d, J = 5.5 Hz)), which requires that one of the vinyl hydrogens be adjacent to a quaternary center and the other be attached to a tertiary center. Two others are eliminated by the observation that pyrolysis of the photoproduct yields a compound containing four vinyl hydrogens (via the 1,5 hydrogen shift characteristic of such vinylcyclopropanes;[6] as expected, the photoproduct from 2-d_2 yields a pyrolysis product with only three vinyl hydrogens). The only remaining options are 13 and 14; though 14 is not excluded by the above facts, it is appreciably more strained than 13. Note that formation of 13 from 2 is formally equivalent to the formation of 5 from 3.

Table I. Effect of 1-Methylcyclohexene (MC) on the 2 → 13 Transformation[a]

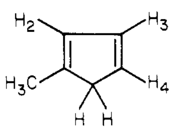
[MC], ×10^{-2} M	loss of 2, ×10^{-3} M	formation of 13, ×10^{-3} M	formation of methylenecyclohexane, ×10^{-4} M
0	1.90	1.26	
0	2.00	1.10	
2.62	1.70	1.34	5.00
2.62	1.70	1.29	6.07

[a] All solutions originally 1.74 × 10^{-2} M of 2 in *t*-butyl alcohol; irradiation time was 2 h.

Photolysis of 13. In any photolysis of 2 there is a gradual buildup of a second photoproduct, 15 (R = H),



15



which time studies readily demonstrated to be a secondary photoproduct and which is quickly formed on photolysis of 13. The cyclopentadiene chromophore is evident in the UV ($\lambda_{\max}$ (hexane) 264 nm (ϵ 2720))[12] and confirmed by the ^{1}H NMR where the cyclopentadiene resonances (δ 6.35 (H$_y$), 6.09 (H$_z$), 5.98 (H$_x$)) and coupling constants (J_{yz} = 5.6, J_{xy} = 2.0, J_{xz} = 1.4 Hz) match up well with those of 1-methylcyclopentadiene (δ 6.25 (H$_3$), 6.07 (H$_4$), 6.0 (H$_2$); J_{34} = 5.4, J_{23} = 1.9, J_{24} = 1.4 Hz).[13] The other vinyl hydrogens of 15 appear as an ABX pattern: δ 5.8–5.4 (1 H, q, J_{AX} = 18, J_{BX} = 9 Hz) and 5.0–4.6 (2 H, J_{AB} = 2 Hz). An additional significant feature is the upfield methyl singlet at δ 0.67 with the remaining signals at δ 2.6–2.4 (2 H, t) and 2.3–1.4 (9 H, m). Photolysis of 2-d_2 gives 15 (R = D) in which the quartet at δ 5.8–5.4 is gone and the signal at δ 5.0–4.6 is simplified and integrates to one proton.

Quantum Efficiencies. These were obtained by irradiation in hexane. Values for formation of 13 were 0.047 and 0.046, or an average of 0.046$_5$. The formation of 15 from 13 was considerably more efficient: 0.50, 0.52, average 0.51.

Quenching Studies. These were carried out on 2 using 1-methylcyclohexene (MC); triplet transfer to this olefin

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[9] E. Wenkert and T. E. Stevens, *J. Am. Chem. Soc.*, 78, 2318 (1956).

[10] Termed "meta" cycloaddition by Bryce-Smith et al; cf. D. Bryce-Smith, W. M. Dadson, A. Gilbert, B. H. Orger, and H. M. Tyrell, *Tetrahedron Lett.*, 1093 (1978).

[11] "Para" (i.e., 1,4) intramolecular cycloaddition has recently been observed for vinyl ethers; cf. ref 3.

[12] Compare L. L. Barber, O. L. Chapman, and J. D. Lassila, *J. Am. Chem. Soc.*, 91, 3664 (1969), in which a 1,1,2-trialkylcyclopentadiene is reported to have $\lambda_{\max}$ (MeOH) 256 nm (ϵ 3850).

[13] V. A. Korenevsky and N. M. Sergeyev, *J. Am. Chem. Soc.*, 94, 8586 (1972).

[14] J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, 1970, p 126. We have confirmed the higher value (0.14) in cyclohexane (p 122).

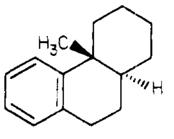
Table II. Fluorescence Quantum Yields and Singlet Lifetimes[a]

compd	ϕ_f[b]	${}^1\tau$, ns[c]
1	0.15	24
16	0.16	22
2	0.14	22
17	0.15	25
18	0.14	24

[a] All solutions are ca. 8×10^{-4} M in hexane; measurements were at room temperature (ca. 23 °C). [b] Data are fully corrected; ϕ_f values are by reference to toluene ($\phi_f = 0.12$)[14] and are ± 0.01. [c] ± 1 ns.

results in formation of methylenecyclohexane, which was monitored by VPC along with **2** and **13**. The data clearly indicate that **13** is singlet derived, though triplet transfer to MC is occurring (cf. Table I).

Spectroscopic Properties of 1 and 2. The ultraviolet absorption spectra of **1** (λ_{max} (hexane) 266 nm (ϵ 427), 274 nm (ϵ 432)) and **2** (λ_{max} (hexane) 266 nm (ϵ 471), 274 nm (ϵ 487)) are quite similar to each other and to the tricyclic arylalkane analogues **16**–**18**. The latter are uniformly slightly lower in their extinction coefficients, however; i.e., for the identically placed maxima, extinction coefficients are 370, 268; 415, 440; and 409, 418 M^{-1} cm^{-1} for **16**, **17**, and **18**, respectively.



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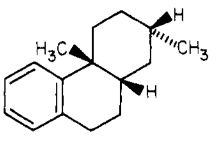

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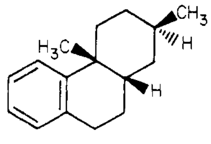

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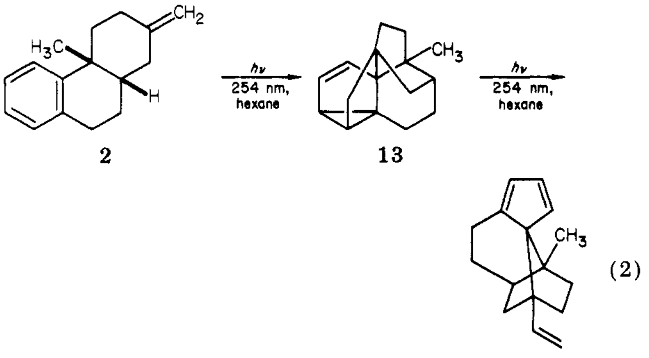
The fluorescence band positions, intensities, and lifetimes are likewise relatively unaffected by the nature of the ring fusion or the presence of the double bond. Emission maxima are 284 nm for **1** and **16** and 283 nm for **2** and **18**. Values for ϕ_f and ${}^1\tau$ are given in Table II.

Neither **1** nor **2** shows phosphorescence at 77 K. Compounds **16**, **17**, and **18** have phosphorescence quantum efficiencies 56, 33, and 23% that of toluene, respectively.

Discussion

A. Singlet Photochemistry and Photophysics. The reactions reported in the Results section are summarized in eq 2. As anticipated, the similarity between conformers **2a** and **3a** surfaces in analogous photochemistry for the two substrates (compare eq 1), and as with the **3** → **4** + **5** transformation, the evidence favors an excited singlet precursor to the photoproduct. Thus, 1-methylcyclohexene, while effectively intercepting the decalin (aryl) triplet (as evidenced by the conversion of 1-methylcyclohexene to methylenecyclohexane),[15] fails to quench the conversion of **2** to **13**.[16] A mechanism analogous to that proposed for **3**[6] appears reasonable (Scheme II; A–O represents the nonconjugated aryl olefin with the chromophores treated as independent entities).[4]



2 13 15 (2)

Scheme II

$$\mathrm{A{-}O} \xrightarrow{h\nu} {}^1\mathrm{A^*{-}O}$$

$${}^1\mathrm{A^*{-}O} \xrightarrow{k_{ic}} \mathrm{A{-}O}$$

$${}^1\mathrm{A^*{-}O} \xrightarrow{k_{isc}} {}^3\mathrm{A^*{-}O}$$

$${}^1\mathrm{A^*{-}O} \xrightarrow{k_{ex}} {}^1(\overset{\frown}{\underset{\smile}{\mathrm{A\quad O}}})^*$$

19 (exciplex)

$$\mathbf{19} \xrightarrow{k_{pdt}} \mathbf{13}$$

$$\mathbf{19} \xrightarrow{k_d} \mathrm{A{-}O}$$

Table III. Comparative Alkene vs. Alkane Photophysical Properties for 2 and 3

	2	17	3	1-phenylhexane
ϕ_f	0.14	0.15	6×10^{-3}	0.13
${}^1\tau$, ns	22.4	25.4	1.0	35.0
k_f, $\times 10^6$ s^{-1}	6.2	5.9	6.0	3.7
k_x, $\times 10^7$ s^{-1}	3.3[b]	3.3[a]	2.5[b]	2.5[a]
ϕ_x	0.74[c]	0.85[a]	0.025[c]	0.87[a]
ϕ_{ex}	0.12[d]		0.97[d]	
k_{ex}, s^{-1} [e]	5.4×10^6		1.0×10^9	
ϕ_{pdt}/ϕ_{ex}	0.39		0.27	

[a] From $\phi_x = \phi_{ic} + \phi_{isc} = 1 - \phi_f$ and $k_x = \phi_x/{}^1\tau$. [b] Assumed to be identical with the alkane value.[2a] [c] From $\phi_x = k_x{}^1r$. [d] From $\phi_{ex} = 1 - (\phi_f + \phi_x)$. [e] From $k_{ex} = \phi_{ex}/{}^1r$.

Despite the above-mentioned similarities in the two (**2**, **3**) substrates, significant differences are also obvious. The quantum efficiency for formation of **13** ($\phi = 0.047$) is fivefold less than was observed for **3** → **4** + **5** ($\phi = 0.26$). This inefficiency is reflected in the fluorescence data; whereas **3** shows a greatly diminished fluorescence yield and lifetime relative to 1-phenylhexane, the data in Table I demonstrate that the photophysical properties of the excited singlet state (^{1}A*–O) of **2** are minimally affected by the double bond. This is best illustrated by the comparative alkene vs. alkane data in Table III. In this table, $k_x = k_{ic} + k_{isc}$ and is assumed to be little affected by introduction of the double bond;[2a] exciplex formation is assumed to be irreversible (the assumption seems justified by the data; see below).

The key number, of course, is k_{ex}. Because of the rapidity of exciplex formation, k_{ex} in compound **3** should correspond to the rate of conformational reorganization about the trimethylene chain to achieve **3a**; it is gratifying that our value of 1.0×10^9 s^{-1} is virtually identical with values obtained by others using charge transfer in photoexcited anthracene-$(CH_2)_3$-*N*,*N*-dimethylaniline[17] and intramolecular excimer formation in 1,3-diphenylpropane.[18]

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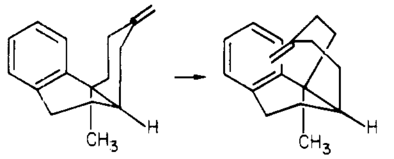
(15) P. J. Kropp, *Pure Appl. Chem.*, **24**, 585 (1970); J. A. Marshall, *Science*, **170**, 137 (1970).

(16) For a similar result in the study of the intramolecular cycloaddition of 6-phenyl-2-hexyne, see W. Lippke, W. Ferree, Jr., and H. Morrison, *J. Am. Chem. Soc.*, **96**, 2134 (1974).

(17) T. J. Chuang, R. J. Cox, and K. B. Eisenthal, *J. Am. Chem. Soc.*, **96**, 6828 (1974).

The rapidity of this rotationally controlled step causes the almost complete elimination of competing radiative and radiationless processes in **3**, with ϕ_{pdt} determined by the ratio of exciplex cycloaddition to exciplex decay (i.e., 27% of the exciplexes go on to product).

For the *cis*-decalin **2**, the rate-controlling conformational reorientation involves the conversion of the half-chair/chair conformer **2b**[19] into the half-chair/boat conformer **2a** (eq 3). Our rate of $k_{ex} = 5.4 \times 10^6$ s^{-1} corresponds to

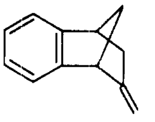


(3)

2b 2a

a $\Delta G^{\ddagger}_{298} = 8.2$ kcal/mol,[20] in excellent agreement with the $\Delta G^{\ddagger}_{160-197} = 8.4$ kcal/mol measured for methylenecyclohexane.[21] The 185-fold reduction in k_{ex} for **2** relative to **3** results in a much reduced effect of exciplex formation on the fluorescence intensity and singlet lifetime of **2**. Note that the ratio of exciplex going on to product has increased by comparison with **3**, from 27% to 39%.

As regards the *trans*-decalin **1**, there is no evidence that the double bond brings about any photochemical or photophysical perturbation of the aryl excited *singlet* state. In previously studied, relatively rigid aryl olefins (e.g., **19** and **20**), we have noted[2a] that the double bond can induce



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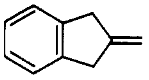

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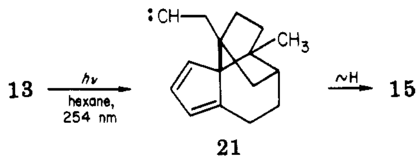
a new, rapid singlet internal conversion mode which appears to involve charge transfer from the double bond to the aromatic ring.[5] We attribute the absence of this decay mode in **1** primarily to the increased separation of the two functionalities (i.e., 4.5 Å for **1** vs. ca. 2.2 Å for **19** and **20**).[22]

B. Interaction in the Triplet State. One intent of our studies on bichromophores has been to delineate the geometrical requirements for intramolecular energy transfer. We therefore find it striking that **1** and **2** show no phosphorescence at 77 K under conditions where intermolecular triplet quenching is demonstrably absent.[23] The observation is significant because intermolecular triplet energy transfer is known to proceed via an orbital-overlap-dependent "exchange mechanism". Thus the 4.5-Å chromophore separation in **1** should be close to the limiting effective quencher/quenchee distance.[24] In fact,

Scheme III



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it is clear that the rate of internal energy transfer in the *cis*-decalin is diminished relative to other aryl olefins we have studied, *for **2** is the first to be capable of intermolecular triplet sensitization in solution* (cf. the sensitized conversion of methylcyclohexene to methylenecyclohexane). Clearly, for **2** (and presumably as well for **1**), internal quenching at room temperature is no longer dominant in the presence of a second reactant, even though phosphorescence is not yet competitive with intramolecular triplet transfer.[25]

C. Further Photolysis of the Cycloadduct 13. The subsequent formation of **15** from **13** is most readily rationalized by a photocycloelimination as outlined in Scheme III. Expulsion of the carbene (**21**), though not hitherto reported for aryl/olefin 1,3 cycloadducts, has some precedent in the recently reported photolysis of a dienylcyclopropane[26] and is well documented for arylcyclopropanes.[27] The unusually high quantum efficiency observed in this case is presumably a consequence of the appreciable strain in **13**.

Conclusions

The photochemical and spectroscopic observations indicate that the rates of singlet and triplet interactions in **1** and **2** are greatly reduced relative to molecules we have previously studied. It is likely that the interchromophore separations in these tricyclics are at the borderline of that which is necessary for effective excited-state perturbations and that molecules containing a modest increase in aryl–olefin distance will exhibit essentially "isolated" chromophore properties. Further studies with molecules containing such increased chromophore separations are in progress.

Experimental Section

The complete experimental details for this work may be found in the Ph.D. Thesis of M.P.[16] The most cogent data are reproduced below. The basic analytical and photochemical techniques and instrumentation have been previously described.[2a] Solvents for photochemical work were Burdick and Jackson "Distilled in Glass"; fluorescence studies employed *n*-hexane and phosphorescence studies used 50:50 *n*-pentane-cyclopentane. Quantum efficiencies were measured using 1-phenyl-2-butene actinometry[28] with column D (105 °C, 72 mL/min, retention times 8.1 and 9.7 min for the trans and cis isomers). Compound **13** was analyzed on column A using *n*-tetradecane as internal standard (140 °C, 40 mL/min, retention times 4.2 and 7.5 min for standard and **13**, respectively). Compound **15** was analyzed under the same conditions using the same standard (retention time 6.4 min). VPC columns were as follows: A, 5 ft × 0.125 in., stainless steel (ss), 10% SE-30 on 100/120 AW-DMCS Chromosorb W; B, 20 ft × 0.125 in., ss, 30% SF-96 on 60/80 AW-DMCS Chromosorb W; C, 20 ft × 0.125 in., ss, 5% XF-1150 on 60/80 AW-DMCS Chromosorb W; D, 12 ft × 0.125 in., ss, 10% AgBF$_4$-20% Carbowax 20M on 100/120 AW-DMCS Chromosorb W; E, 20 ft ×

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(18) W. Klöpffer and W. Liptay, *Z. Naturforsch. A*, **25**, 1091 (1970).

(19) Conformer **2b** puts the methyl group equatorial to ring C, and thus minimizes 1,3-diaxial CH$_3$/H interactions.

(20) Calculated using a transmission coefficient of 1.0. If a value of 0.5 is used, then $\Delta G^{\ddagger}$ becomes 7.8 kcal/mol (cf. D. K. Dalling, D. M. Grant, and L. F. Johnson, *J. Am. Chem. Soc.*, **93**, 3678 (1971).

(21) J. T. Gerig and R. A. Rimerman, *J. Am. Chem. Soc.*, **92**, 1219 (1970).

(22) Recognizing, of course, that this singlet interaction has also shown some dependence on the relative disposition of the two groups in space.[2a] The dicyanoethylene analogue of **1** does show a charge-transfer absorption band at 300 nm (compare P. Pasman, J. W. Verhoeven, and T. J. DeBoer, *Chem. Phys. Lett.*, **59**, 381 (1978).

(23) Such has been the case for every nonconjugated aryl olefin we have studied to date.

(24) A. A. Lamola in "Organic Photochemistry and Energy Transfer", A. A. Lamola and N. J. Turro, Eds., Interscience, New York, 1969. See also the lucid discussion in N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings, Menlo Park, CA, 1978, Chapter 9.

(25) Preliminary studies indicate this also to be the case for the internal olefins 7,4bβ-dimethyl-4bβ,5,8,8aα,9,10-hexahydrophenanthrene and its 8aβ isomer.

(26) R. G. Weiss and G. S. Hammond, *J. Am. Chem. Soc.*, **100**, 1172 (1978).

(27) G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, **10**, 537 (1972).

(28) H. Morrison, J. Pajak and R. Peiffer, *J. Am. Chem. Soc.*, **93**, 3978 (1971); H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968).

0.25 in, aluminum, 10% SE-30 on 40/60 AW-DMCS Chromosorb.

7-Methylene-4bβ-methyl-4bβ,5,6,7,8,8aα,9,10-octahydrophenanthrene (1). The reaction vessel used was a 100-mL three-necked round bottom containing a magnetic stirring bar with a gas inlet, outlet tube, and a condenser. To a slurry of 988.0 mg (2.444 mmol), a 29.2% excess, of triphenylmethylphosphonium iodide in 45 mL of THF was added 1.2 mL of 2 M (2.4 mmol) *n*-BuLi in *n*-hexane. After stirring for 15 min, all of the solid had dissolved, and the solution had turned the characteristic red. Then 405.1 mg (1.891 mmol) of the saturated trans ketone, dissolved in 20 mL of dry THF, was added dropwise via syringe. The solution turned a yellowish orange color. The reaction was refluxed overnight.

The reaction mixture was transferred to a round bottom, and the solvent was taken off on the rotary evaporator at 40–50 °C. The wet solid, weighing 351.1 mg, was placed on 35.6 g of silica gel and eluted with petroleum ether. A sweet smelling odor followed soon after the solvent front. The separation was followed on column C (156 °C, 240 mL/min, retention time 22 min). Distillation at 105 °C (0.6 mm) yielded 392 mg (97.8%) of product: IR (neat) 3.25, 3.40, 6.07, 6.68, 6.90, 7.01, 7.29, 8.50, 8.70, 9.41, 9.49, 9.81, 11.30, 13.25, and 13.99 μm; NMR ($CDCl_3$) δ 6.95–7.36 (m, aryl, 4 H), 4.61 (s, olefinic, 2 H), 2.75–2.96 (t, benzylic 2 H), 1.38–2.47 (m, 14 H, including the angular methyl singlet at 1.13); mass spectrum (70 eV) (*m/e*) 212 (M^+) and 197 (base ion). Anal. ($C_{16}H_{20}$) C, H.

7-Methylene-4bβ-methyl-4bβ,5,6,7,8,8aβ,9,10-octahydrophenanthrene (2). Using precisely the same procedure on the cis ketone as that which was used for the trans, 1.04 g of the cis ketone was converted into 1.03 g (99.9%) of the product: the compound was distilled at 105 °C (0.6 mm Hg): IR (neat) 3.38, 6.06, 6.76, 6.84, 6.96, 7.00, 11.35, 13.31, and 13.73 μm; NMR ($CDCl_3$) δ 6.92–7.38 (m, aryl, 4 H), 4.57 (s, olefinic, 2 H), 2.65–2.93 (m, benzylic, 2 H); mass spectrum (70 eV) (*m/e*) 212 (M^+) and 117 (base ion). Anal. ($C_{16}H_{20}$) C, H.

7-(Methylene-d_2)-4bβ-methyl-4bβ,5,6,7,8,8aβ,9,10-octahydrophenanthrene (2-d_2). This compound was prepared in a fashion analogous to that used to prepare the undeuterated sample, utilizing (methyl-d_3)triphenylphosphonium iodide. The desired olefin was greater than 90% deuterated by integration of the olefinic region in the NMR. The yield was 71%. The spectral data are as follows: IR (neat) 3.29, 3.41, 3.48, 6.16, 6.72, 6.92, 7.29, 13.18, 13.75, 13.92, and 14.41 μm; NMR ($CDCl_3$) δ 6.92–7.38 (m, aryl, 4 H), 2.65–2.93 (m, benzylic, 2 H), 1.46–2.48 (m, 9 H), 1.29 (s, angular methyl, 3 H); mass spectrum (70 eV) (*m/e*) 214 (M^+) and 128 (base ion).

4bβ-Methyl-4bβ,5,6,7,8,8aα,9,10-octahydrophenanthrene (16).[29] Technical grade zinc powder was activated by washing with 2% HCl for 3–4 min and then successively with three 20-mL portions of H_2O, ethyl alcohol, acetone, and dry ether. The powder thus obtained was warmed to 60 °C under reduced pressure for 5 min and kept in a sealed flask at room temperature for 1 day. A 156.0-mg sample of 12 was dissolved with stirring in 13 mL of acetic anhydride saturated with hydrochloric gas at 0 °C. The solution took on a shade of yellow. Active zinc powder (0.7 g) was added to the resulting solution and allowed to stir for 15–20 min, after which the temperature was gradually raised to room temperature. The mixture was stirred at room temperature for 17 h and then poured into 125 mL of water. The aqueous solution was made basic with sodium carbonate and thoroughly extracted with ether (4 × 50 mL). The combined ethereal fractions were washed once with 50 mL of brine and dried over Na_2SO_4, and the solvent was removed on the rotary evaporator at 30–40 °C to give a brown oil which was chromatographed on 4 g of silica gel. The product (29.0 mg) was obtained analytically pure by VPC, column A (170 °C, 48 mL/min, retention time 5 min); IR (neat) 3.39, 6.75, 6.84, 6.95, 7.33, 9.40, 9.68, 13.26, and 13.91 μm; NMR ($CDCl_3$) δ 6.94–7.33 (m, aryl, 4 H), 2.70–2.98 (m, benzylic, 2 H), 1.14–2.35 (m, 11 H), 1.06 (s, angular methyl, 3 H); calcd for $C_{15}H_{20}$, *m/e* 200.157; found, *m/e* 200.156.

(7α and 7β),4bβ-Dimethyl-4bβ,5,6,7,8,8aβ,9,10-octahydrophenanthrenes (17 and 18). An 80-mg sample (0.377 mmol) of 2 was hydrogenated in the Brown[2] hydrogenator. The compound was dissolved in 20 mL of ethanol containing 80 mg of 10% Pd(C) and hydrogenated for 6 h. Upon filtration and removal from the solvent, the components were separated by VPC on column E (180 °C, 48 mL/min) to give 12.1 mg of the first peak (**17**) and 17.5 mg of the second (**18**) for a total yield of 37%. The assignment of structure of these two isomers rests on the higher upfield shift of the 7α-methyl of **17** (δ 0.74) relative to the 7β-methyl of **18** (δ 0.92) presumed to be caused by the closer aproach of the 7α-methyl to the aromatic ring.

17: IR (neat) 3.30, 3.43, 3.49, 6.71, 6.88, 6.95, 7.28, 13.19, and 13.75 μm; NMR ($CDCl_3$) δ 6.97–7.35 (m, aryl, 4 H), 2.65–2.95 (m, benzylic, 2 H), 1.93–2.52 (m, 2 H), 0.84–1.73 (m, 11 H including the angular methyl at 1.14), 0.74 (d, *J* = 6 Hz, 3 H); mass spectrum (70 eV), *m/e* 214 (M^+). Anal. ($C_{16}H_{22}$) C, H.

18: IR (neat) 3.46, 3.51, 6.71, 6.85, 6.96, 7.30, 9.22, 9.67, 12.71, 13.23, and 13.70 μm; NMR ($CDCl_3$) δ 6.93–7.33 (m, aryl, 4 H), 2.67–2.88 (m, benzylic, 2 H), 1.0–2.1 (m, 13 H including the angular methyl at 1.33), 0.92 (d, *J* = 6 Hz, 3 H); mass spectrum (70 eV), *m/e* 214 (M^+). Anal. ($C_{16}H_{22}$) C, H.

Isolation of 13 and 15. A solution of 2 (500 mg, 2.36×10^{-2} M) in hexane was degassed with argon and irradiated for 4 h at 254 nm in a photolysis well. The solvents were evaporated in vacuo and the photoproducts were separated on column E (180 °C, 30 mL/min, retention times 10, 11, and 19 min for **15**, **13**, and **2**, respectively).

13: IR (neat) 3.24, 3.37, 6.74, 6.83, 7.19, 13.20, and 13.85 μm; NMR ($CDCl_3$) δ 5.65–5.80 (dd, vinyl, *J* = 2.0 and 5.5 Hz, 1 H), 5.45–5.60 (d, vinyl, *J* = 5.5 Hz, 1 H), 0.8–2.3 (complex, including a singlet at δ 0.98, 18 H). Anal. ($C_{16}H_{20}$) C, H.

15: IR (neat) 3.25, 3.42, 6.10, 6.53, 6.85, 6.94, 7.30, 10.05, 10.95, 11.15, 11.30, 13.95, and 14.30 μm; NMR ($CDCl_3$) δ 6.35 (dd, vinyl, *J* = 5.4 and 2.0 Hz, 1 H), 6.09 (dd, vinyl, *J* = 5.4 and 1.4 Hz, 1 H), 5.98 (dd, vinyl, *J* = 2.0 and 1.4 Hz), 5.4–5.8 (q, vinyl, *J* = 17.7 and 10.2 Hz, 1 H), 4.6–5.0 (m, vinyl, *J* = 2, 10.2, and 17.7 Hz, 2 H), 2.4–2.6 (t, 2 H), 1.4–2.3 (m, 9 H), and 0.67 (s, 3 H). Anal. ($C_{16}H_{20}$) C, H.

Hydrogenation of 13. Compound 2 was used to determine how much hydrogen could be evolved from 1.00 mL of $NaBH_4$ solution (unstandardized) using the Brown[2] hydrogenator. A 127.6-mg sample (0.598 mmol) of 2 required 4.39 mL of $NaBH_4$ solution, which meant that each milliliter of this solution liberated 0.136 mmol of hydrogen.

A 60.5-mg sample (0.285 mmol) of 13 in 40 mL of EtOH with 115 mg of 10% Pd/C was treated with the above $NaBH_4$ solution. After 18 h, no further uptake of hydrogen was observed; a total of 4.19 mL of $NaBH_4$ solution (0.570 mmol of H_2) was consumed. The product (34.7 mg, 0.161 mmol, 56.5%) was obtained after filtration of the catalyst and removal of the solvent on the rotary evaporator 40–60 °C. An analytical sample was prepared on column E (180 °C, 60 mL/min, retention time 8 min): IR (neat) 3.45, 6.85, 7.29 μm; NMR ($CDCl_3$) δ 0.60–2.10 (m, including a singlet at δ 0.92). Anal. ($C_{16}H_{24}$) C, H.

Pyrolysis of 13. About 30 mg (0.14 mmol) of 13 was sealed in a glass tube and heated in a VPC oven at 300 °C for 20 min. Though considerable charring occurred, a small amount of pyrolysate could be purified on column E (170 °C, 60 mL/min, retention time 8 min); the olefin region in the NMR gave signals at ($CDCl_3$) δ 5.87 (d, 1 H), 5.56 (s, 2 H) and 5.32 (d, 1 H). Pyrolysis of 13-d_2 gave a crude sample with ($CDCl_3$) δ 5.56 (s, 2 H) and 5.32 (s, 1 H).

Preparation of 13-d_2 and 15-d_2. The reaction and isolation procedure were identical with that for **13** and **15**.

13-d_2: NMR ($CDCl_3$) δ 5.65–5.80 (dd, vinyl, *J* = 2.0 and 5.5 Hz, 1 H), 5.45–5.60 (d, vinyl, *J* = 5.5 Hz, 1 H), 0.8–2.3 (complex, including a singlet at δ 0.98, 16 H).

15-d_2: NMR ($CDCl_3$) δ 6.35 (dd, vinyl, *J* = 5.4 and 1.9 Hz, 1 H), 6.09 (dd, vinyl, *J* = 5.4 and 1.4 Hz, 1 H), 5.98 (dd, vinyl, *J* = 1.9 and 1.4 Hz, 1 H), 2.4–2.6 (t, 2 H), 1.4–2.3 (m, 9 H), and 0.67 (s, 3 H).

Photolysis of 2 in the Presence of 1-Methylcyclohexene (MC). Four solutions of 1.74×10^{-2} M 2 in *t*-butyl alcohol, two containing 2.62×10^{-2} M MC and all containing 1.25×10^{-2} M *n*-heptadecane, were degassed with argon for 20 min and irradiated for 2 h at 254 nm in 10-mL quartz photolysis tubes at ambient temperature in a turntable. 2 and its photoproduct were analyzed on column C (152 °C, 20 mL/min, retention times 4.7, 7.5, and

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[29] The method is that of S. Yamamura and Y. Hirata, *J. Chem. Soc. C*, 2887 (1968).

21.8 min for standard, **13**, and **2**, respectively). MC and its isomer were analyzed on column B (140 °C, 19 mL/min, retention time 8.1, 9.0, and 15.9 for methylenecyclohexane, MC, and nonane (standard), respectively).

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Registry No. **1**, 72541-64-1; **2**, 68613-81-0; **2**-d_2, 72541-65-2; **3**, 23086-43-3; **11**, 6606-34-4; **12**, 1686-50-6; **13**, 68613-82-1; **13**-d_2, 72541-66-3; **15**, 68613-84-3; **15**-d_2, 72541-67-4; **16**, 70561-39-6; **17**, 72541-68-5; **18**, 72541-69-6; *cis*-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-one, 70524-91-3.

A New Synthesis of α-Tocopherol

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α-Tocopherol (vitamin E, **1**) has been synthesized in racemic form following a new strategy in which the aromatic ring of the chroman is constructed by addition of the dianion of 2,4-pentanedione to 1,2-epoxy-2,6,10,14-tetramethylpentadecane (**5**) as a side-chain precursor, followed by condensation with dimethyl acetonedicarboxylate and reduction to the key "tocopherylphenol" **8**. Oxidation of **8** with a new organic-soluble bis(quaternary ammonium) salt of Fremy's radical gives tocopherylquinone (**9**), a known precursor of α-tocopherol (**1**).

α-Tocopherol (vitamin E, **1**) has been the synthetic objective of several recent studies directed especially toward the synthesis of the natural product, (2*R*,4′*R*,8′*R*)-α-tocopherol.[2] The renewed interest in this vitamin is due in part to the increasingly apparent biological importance of vitamin E[3] and in part to the development of new synthetic methods for the synthesis of the chiral centers in the side chain[4] and chroman[5] portions of the molecule. The reported approaches[2] have been based on the coupling of chroman and side-chain moieties or on elaboration of preformed chroman units.

We envisioned a strategy in which the chroman ring could be constructed from simple aliphatic precursors starting from a functionalized, potentially chiral side chain or side-chain segment.[6] The approach (Scheme I) using an epoxide (**2**) as this segment to form O-1, C-2, and C-3 of the chroman ring, and 2,4-pentanedione and a 3-pentanone equivalent for the remaining atoms, seemed to be a particularly direct route to **1** via the phenol **3**. We now report our investigations in the racemic series[7] (Scheme II), leading to a synthesis of the previously unknown "tocopherylphenol" (**8**) and its oxidation by a new organic-soluble version of Fremy's salt[9] to tocopherylquinone (**9**), a well-known precursor[2a] of **1**.

Scheme I

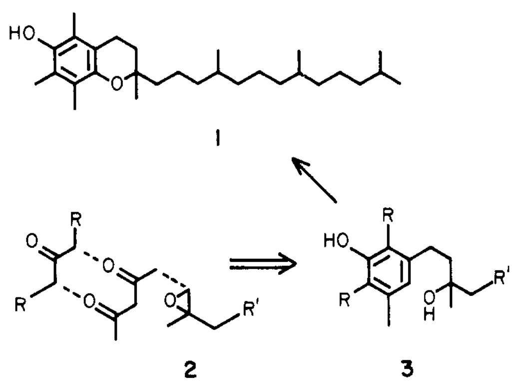

Table I. Oxidation of Phenol 8 under Phase-transfer Conditions

expt	$ON(SO_3K)_2$, mmol[a]	phenol 8, mmol	ammonium salt 10, mmol[b]	time to completion[c]
1	0.54	0.23	0.043	5 h
2	0.54	0.23	0.21	2-3 h
3	0.54	0.23	0.43[d]	20 min
4	0.54	0.23	0.84	20 min

[a] The concentration of the solution was determined to be 0.175 M by measurement of the absorption at 440 nm where Fremy's salt has $\epsilon = 14.5$. [b] Commercial **10** has a mixture of C_8 and C_{10} alkyl groups. The molecular weight of the predominant $(C_8H_{17})_3NCH_3Cl$ species is used for the calculation. [c] Judged by TLC. [d] Shows some purple color in the organic phase.

Results

Hexahydrofarnesylacetone (**4**) was converted to the oily epoxide **5** in 92% yield by methylenation with tri-

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[1] Synthetic Chemicals Division, Eastman Kodak Co., Rochester, NY 14650.

[2] For recent reviews see (a) H. Mayer and O. Isler, *Methods Enzymol.*, **18**, Part C, 241 (1971); (b) S. Kasparek in "Vitamin E", L. J. Machlin, Ed., Marcel Dekker, New York, 1979, Chapter 2; (c) J. M. Akkerman, H. deKoning, and H. O. Huisman, *J. Chem. Soc., Perkin Trans. 1*, (1979); (d) C. Fuganti and P. Grasselli, *J. Chem. Soc., Chem. Commun.*, 995 (1979).

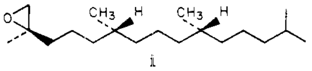
[3] (a) J. G. Bieri and P. M. Farrell, *Vitam. Horm.* **34**, (N.Y.), 31 (1976); (b) Chapters 1, 3–12 in ref **2b**.

[4] See ref 3 in ref **5a**.

[5] (a) N. Cohen, R. J. Lopresti, and G. Saucy, *J. Am. Chem. Soc.*, **101**, 6710 (1979); (b) N. Cohen, J. W. Scott, F. T. Bizzarro, R. J. Lopresti, W. F. Eichel, G. Saucy, and H. Mayer, *Helv. Chim. Acta*, **61**, 837 (1978).

[6] Related approaches have been studied in several Roche laboratories: (a) see ref **5a**; (b) H. G. W. Leuenberger, W. Boguth, R. Barner, M. Schmid, and R. Zell, *Helv. Chim. Acta*, **62**, 455 (1979); (c) M. Schmid and R. Barner, *ibid.*, **62**, 464 (1979); (d) R. Zell, *ibid.*, **62**, 474 (1979); (e) R. Barner and M. Schmid, *Helv. Chim. Acta*, **62**, 2384 (1979).

[7] A stereospecific synthesis of racemic i from hydroxyacetonide ii (derivable[8a,b] from citramalic acid (the *R* isomer[8c] would be needed for natural α-tocopherol)) will be reported in due course.



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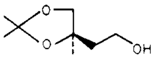

ii

[8] (a) P. A. Stadler, A. J. Frey, and A. Hofmann, *Helv. Chim. Acta*, **46**, 2300 (1963); (b) H. K. Spencer, H. N. Khatri, and R. K. Hill, *Bioorg. Chem.*, **5**, 177 (1976); (c) T. Sai, K. Aida, and T. Uemura, *J. Gen. Appl. Microbiol.*, **15**, 345 (1969).

[9] (a) G. L. Olson and G. Saucy, U.S. Patent 4127608, 1979; (b) H.-J. Teuber and W. Rau, *Chem. Ber.*, **86**, 1036 (1953); (c) P. A. Wehrli and F. Pigott, *Org. Synth.*, **52**, 83 (1972).

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