(6) This phenomenon differs from exciplex substitution: H. Ohta, D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *J. Am. Chem. Soc.*, **98**, 2002 (1976).
(7) Concentration dependence plots were regular but not linear for DCB and CA sensitizers (intercepts ~ 1.0). DCB and HMDB were competitive absorbers at even a choice wavelength (288 nm) and CA underwent competitive photodecomposition (dimerization[8]), especially at low concentrations of HMDB. Irradiations for all sensitizers were carried out using a monochromator: 288 (DCB), 313 (CN), and 366 (DCA, CA) nm.
(8) T. Sasaki, K. Kanematsu, I. Ando, and O. Yamashita, *J. Am. Chem. Soc.*, **99**, 871 (1977).
(9) Exciplex fluorescence maxima for quenching by HMDB or HMB in cyclohexane are as follows: DCB, 392; CN, 373; DCA, 500; CA, 450 nm. The CA–HMDB exciplex emission is very weak and poorly resolved; the corresponding CA–HMDB exciplex fluorescence is not detectable.
(10) HMB was not detected (<0.5%) in purified samples of HMDB before or after fluorescence measurements. Since quenching efficiencies for HMDB and HMB are similar (Table I), the portion of the observed emission on HMDB quenching which is due to competitive HMB quenching must be negligible.
(11) R. A. Caldwell, D. Creed, and H. Ohta, *J. Am. Chem. Soc.*, **97**, 3246 (1975).
(12) HMDB was found to be a quencher of CN–HMB exciplex fluorescence ($k_q\tau$ = 35 M^{-1}). Indeed the CN–HMDB-derived emission reaches a limiting value and diminishes at high concentrations of HMDB. Values of $k_q\tau$ for DMH quenching of the CN–HMDB derived emission were obtained at several concentrations of HMDB and extrapolated to [HMDB] = 0 to obtain the value of 49 M^{-1}.
(13) Relative quantum yields for isomerization in the presence of DMH were corrected for the amount of quenching due to interception of CN singlets, (DMH quenching of CN fluorescence). The residual isomerization quenching ($k_q\tau$ = 5.3 M^{-1} after correction) appears to be real and can be associated with DMH interception of the apparently shorter lived CN–HMDB exciplex which is responsible for rearrangement. Taylor has obtained spectroscopic evidence for the CN–HMDB exciplex in low temperature experiments.[5]
(14) (a) Relatively low yields of HMB exciplex emission do not allow a decisive test. The quantum yield of exciplex fluorescence for CN–HMB is 0.1. The adiabatic fluorescence yield then for the CN–HMDB pair is 0.02. Absolute fluorescence yields for the other exciplex pairs are similarly low. (b) We believe it unlikely that radical-ion formation (and the chain propagation of rearrangement observed in methanol[4]) is important in cyclohexane. The solvent dependent behavior of exciplexes of HMB (which has electron-donor properties similar to HMDB) provides support. HMB exciplexes are highly emissive in cyclohexane but nonemissive in acetonitrile showing a resistance to ionic photodissociation[15] in the nonpolar solvent. Geminate sensitizer–HMDB radical-ion pairs capable of rearrangement and back-electron transfer in a solvent cage cannot be excluded.
(15) (a) H. Akazawa, T. Hino, and N. Mataga, *J. Phys. Chem.*, **79**, 994 (1975); (b) T. Hino, H. Akazawa, and N. Mataga, *ibid.*, **80**, 33 (1976).
(16) N. J. Turro, V. Ramamurthy, and T. J. Katz, *Nouv. J. Chim.*, **1**, 363 (1977).
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(18) For example, 1,4-dimethoxyanthracene (DMA) is a DHD → DTP sensitizer ($\phi_{lim} \simeq 0.2$). Quenching of DMA fluorescence by DTP results in exciplex fluoresence (λ_{max} 460 nm). This emission is not observed on quenching DMA by DHD.

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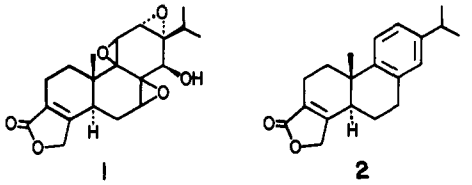
Isodehydroabietenolide

Sir:

In synthetic approaches to the promising anti-leukemic agent triptolide (**1**), as well as other natural products with the novel 18(4→3)*abeo*-abietane skeleton,[1a] such as stemolide,[1b] lactone **2** (or a close relative thereof) is anticipated to be a pivotal intermediate, pathways to which can be rocky because of the greater thermodynamic stability of the A/B cis arrangement in this system.[2] Herewith we describe two, distinctly dissimilar routes to this A/B trans tetracyclic prototype ("isodehydroabietenolide"): one features an electrocyclic reaction involving transformation of an allylic sulfonium methylide to a butenyl sulfide, and the other depends on a polyene cyclization initiated by a β-keto ester unit, a new version of this reaction type.



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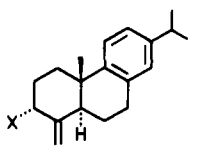
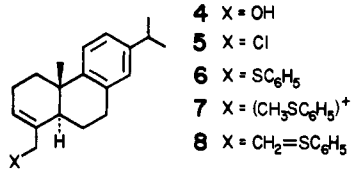
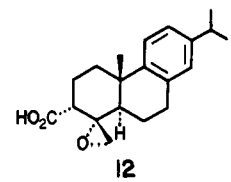


3 X = H
9 X = $CH_2SC_6H_5$
10 X = CHO
11 X = COOH

In the first approach, which requires isolation and purification of only three intermediates, the known dehydroabietene **3** serves as the starting material, accessible by a totally synthetic route terminating with cyclization of a polyene ketone,[3] or better by a previously described pathway starting from dehydroabietic acid.[6] On treatment with i-Pr_2NAlEt_2[7] in benzene–petroleum ether at 50 °C for 2 days, the known[8] α-epoxide of **3** was converted into the allylic alcohol **4**; 60-MHz



4 X = OH
5 X = Cl
6 X = SC_6H_5
7 X = $(CH_3SC_6H_5)^+$
8 X = $CH_2{=}SC_6H_5$



12

NMR (CCl_4), inter alia, δ 3.98 (dd, J = 14 Hz, 2 H, 19-CH_2), 5.63 (s, 1 H, 3-CH). The Lees reagent (n-Bu_3P-CCl_4) was used for formation of allylic chloride **5**, which was transformed by means of $LiSC_6H_5$ in THF at room temperature to thioether **6** (78% from **3**, without isolation of intermediates). The product of S-methylation ($Me_3O^+BF_4^-$ in CH_3CN at 0 °C), sulfonium salt **7**, was deprotonated (BuLi in THF, −78 → 0 °C) to give the corresponding methylide (**8**) which, via a [2,3]-sigmatropic shift,[9] isomerized to the butenylic thioether **9** (86% from **6**). After monochlorination of the S-methylene moiety (N-chlorosuccinamide in CCl_4), exposure to methanol at 0 °C followed by $I_2/NaHCO_3$ in dioxane–water resulted in formation of aldehyde **10** (63% from **9**).

The synthesis can be completed without further isolation of intermediates. After oxidation of **10** to acid **11** ($NaClO_2/NH_2SO_3H$ in dioxane–water at room temperature)[10] (NMR (CCl_4), inter alia, β 3-CH, δ 3.30 ($w_{h/2}$ = 7 Hz)), 3,5-dinitroperbenzoic acid[11] in methylene dichloride at room temperature was employed for conversion into epoxy acid **12.** The corresponding methyl ester, through the action of lithium diisopropylamide (THF, −78 °C → room temperature), suffered β-elimination and lactonization, providing (50% from **10**) lactone **2** as a viscous oil; M^+ 296; IR^{NaCl} 1748 (C=O), 1669 cm^{-1} (conjugated C=C); NMR (CCl_4), inter alia, δ 1.02 (s, 3 H, 20-CH_3), 1.20 (d, J = 6.5 Hz, 6 H, 16-CH_3 and 17-CH_3), 4.65 (m, 2 H, 19-CH_2), 6.80–7.30 (m, 3 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 70.1 (C-19), 124.4 (C-3), 162.6 (C-4), 173.5 (C-18); UV λ_{max} 216 nm (EtOH, ε 19 900). In respect to the lactone and A-ring moieties, the IR, UV, and ^1H NMR spectra of **2** thus compare favorably with those of triptolide itself:[1a] IR^{KBr} 1773 (C=O), 1686 cm^{-1} (C=C); NMR ($CDCl_3$) δ 4.78 (m, 2 H, 19-CH_2); λ_{max} 218 nm (EtOH, ε 14 000). Similarly, the ^{13}C NMR correlates impressively with that of stemolide:[1b] δ 70.2 (C-19), 124.3 (C-3), 162.0 (C-4), 173.5 (C-18). Isodehydroabietenolide obtained as described above was identical in all respects with A/B trans material and dissimilar to the A/B cis isomer, both obtained from dehydroabietic acid by entirely independent means currently being developed and improved in this laboratory.

In preliminary studies involving a fundamentally different synthetic approach, the substituted acetoacetic ester **13** was constructed and subjected to carbocyclization conditions. Reaction of the Grignard reagent (Mg/THF) of m-isopropyl-β-phenethyl bromide[12] with α-methylcyclopropane car-

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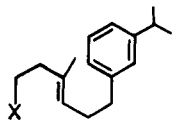
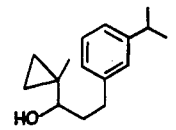


13 X = $CH(COCH_3)COOCH_3$
15 X = Br



14

boxaldehyde led to the cyclopropylcarbinol **14,** which was converted[13] into homoallylic bromide **15.** Alkylation of methyl acetoacetate with **15** gave **13,** which, on treatment with $SnCl_4/CH_2Cl_2$ at room temperature was transformed into the methyl ester of the racemic form of β,γ-unsaturated acid **11,**[14] an intermediate in the lactone **2** synthesis described above. As far as we are aware, this polyene cyclization represents the first case in which a β-keto ester unit acts as the initiator.[15,16]

Acknowledgments. The authors are grateful to the American Cancer Society for grant support (CH-48) and to R. G. Hoffmann of the Resins Division of the Organic Department, Hercules Inc., for a generous gift of pine rosin.

References and Notes

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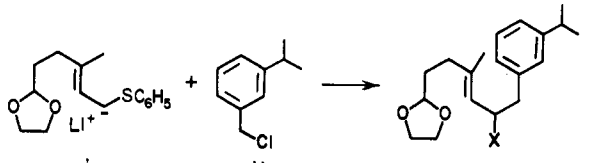
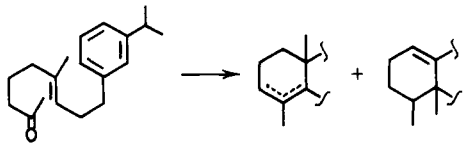
(2) As indicated by the base-induced conversion of **2** into the cis isomer (unpublished observation by Mr. J. Demers in this laboratory) as well as the exclusive formation of cis hydroxyamide by lactone ring opening of **2.**
(3) In this approach, thioether anion i was alkylated with benzyl halide ii,[4] yielding sulfide iii (X = SC_6H_5), which was reductively desulfurized with



i ii iii

Ca/NH_3 to iii (X = H). Conversion of the latter into aldehyde was followed by treatment with $(C_6H_5)_3PC(OMe)CH_3$,[5] giving after hydrolysis ketone iv. Cyclization was carried out with $SnCl_4$ in methylene chloride, providing (50%) isomeric olefins in the ratio **3**:v:vi = 1:5:3.



iv v vi

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(12) Obtained by reaction in THF of *m*-isopropenylphenylmagnesium bromide with ethylene oxide, followed by hydrogenation (Pd/C, EtOH) and Lees reaction with $CBr_4(C_6H_5)_3P$ in CH_3CN.
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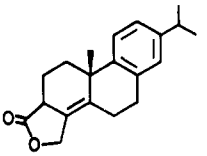
(14) Congeners have been tentatively identified as the ($\Delta^{4(5)}$ ester and the 3-carbomethoxyl counterpart of structure vi.[3]
(15) For previous contributions toward the synthesis of the triptolide system, especially the hydroxy triepoxide moiety, see (a) F. T. Sher and G. A. Berchtold, *J. Org. Chem.*, **42,** 2569 (1977); (b) H. Koike and T. Tokoroyama, *Tetrahedron Lett.*, 4531 (1978); (c) D. Frieze and G. A. Berchtold, *ibid.*, 4607 (1978).
(16) After the submission of this communication, there appeared a publication by H. Koike and T. Tokoroyama, *Chem. Lett.*, 333 (1979), claiming the synthesis of tetracycle **2.** However, the spectral properties of their lactone are very different from those exhibited by our samples of **2** as well as the A/B cis counterpart, but are consistent with its formulation as vii.



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(17) NSF Fellow, 1975–1978.

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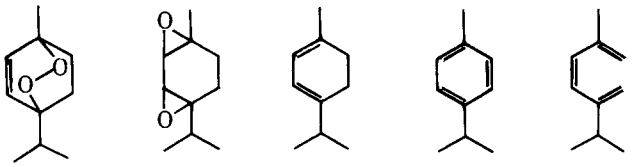
Organic Photochemistry with 6.7-eV Photons: Ascaridole[1]

Sir:

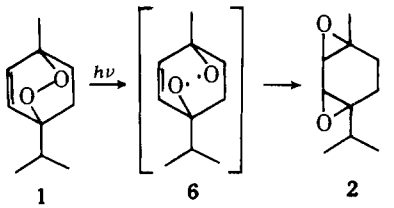
The ultraviolet absorption spectrum of ascaridole (**1**)[2] has not only a long, low-intensity absorption extending to 360 nm



1 2 3 4 5

as in other peroxides,[3] but also a maximum at 233 nm (ϵ 166). It has been conjectured[2] that this "presumably implies interaction of the oxygen lone pairs with the double bond, perhaps in the antibonding orbital". The irradiation of this compound at 185 nm was of interest since such photon energy (6.7 eV) would correspond to the $\pi \rightarrow \pi^*$ absorption of the olefinic group. Studies on photochemistry of bichromophoric systems in the far-ultraviolet are few. Such studies would serve to answer the question if intramolecular coupling between chromophores in the excited states can be observed in the lifetimes of the excited states which tend to be quite short in the far-ultraviolet region.

In an earlier study of the photochemistry of ascaridole with light of wavelength >300 nm,[2] it was found that the only product was isoascaridole (**2**) which was formed in high yield. The reaction **1** → **2** was slow on direct irradiation, but was speeded up significantly when triplet sensitizers were used. The primary reaction (eq 1) was suggested[2] to involve cleavage to



1 6 2 (1)

the diradical **6,** a process that would be consistent with the photochemistry of peroxides at long wavelengths.[3]

Photolysis of ascaridole of 185 nm in hydrocarbon solution[4] gave isoascaridole (**2**), α-terpinene (**3**), the triene **5,** a trace of *p*-cymene (**4**), and oxidation products derived from the solvent which were cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone when the solvent was cyclohexane. At low con-

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