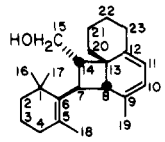
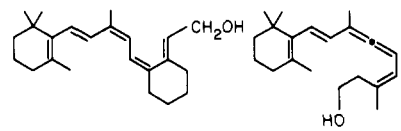
allene **7b** (43% based on **9b**).[11]

The thermally induced rearrangement of the vinylallenol **7b** (10^{-3} M in purified hexanes at reflux, ~69 °C, 4 h) followed by preparative HPLC afforded four components (82% mass balance) in the following order of elution: a substance characterized as **11** (12%) and the 12-s-cis-locked retinols, 11-*cis*,13-*cis*-**4b** (33.1%),





11 12 13

11-*cis*-**3b** (13.5%), and 9-*cis*,11-*cis*,13-*cis*-**5b** (22.8%). Each of the four thermolysis products was individually subjected to the conditions of thermolysis (refluxing hexanes, 4 h) and found to be unchanged by ^{1}H NMR and HPLC analyses.

The observation of **11** as one of the thermolysis products of **7b** is of particular interest since no retinol possessing the 9-cis,11-cis geometry was observed as a product in the thermolysis of the previously reported vinylallenol **13**.[4a] Structure **11** is proposed on the basis of spectral analysis[11] and on the reasonable mechanistic hypothesis that it can be derived from further rearrangement of the putative 9-cis,11-cis-isomer **12**. Examination of **12** reveals in it the presence of *trans*,*cis*,*cis*,*trans*-octatetraene moiety. Such tetraenes are known to undergo extraordinarily facile eight-electron conrotatory electrocyclization to cycloocta-1,3,5-trienes, which further electrocyclize to bicyclo[4.2.0]octa-2,4-dienes in a six-electron disrotatory manner.[12] A similar series of tandem electrocyclizations should result in the rearrangement of the putative intermediate **12** to **11**.

The retinol analogues **3b**, **4b**, and **5b** are considered to be of the 11-cis geometrical series on the basis of their method of synthesis via the thermal [1,5] sigmatropic rearrangement. The 13-cis geometry for **4b** and **5b** was based on observation of an NOE between H_{15} and H_{10} in these isomers while no NOE was observed between these protons in **3b**. Compound **5b** was assigned the 9-cis geometry on the basis of deshielding of H_8 (~0.6 ppm) as a result of interaction with H_{11}.[11,13] The retinols were individually oxidized (MnO_2, low-boiling petroleum ether, 0 °C, 1 h; ~80%) to the corresponding retinals, and the spectral data for these compounds were also in accord with the assigned geometries.[11]

The electronic absorption spectra of retinals generally exhibit prominent α bands (~360 nm) and weak β bands (~280 nm).[14] In striking contrast, the absorption spectra of the 12-s-cis-locked retinal analogues show marked enhancements of the β bands relative to the α bands,[11] a phenomenon also exhibited by 9-*cis*,11-*cis*,13-*cis*-retinal.[4a] Interestingly, the corresponding 12-s-trans-locked analogues exhibit maxima in the α region.[5] It thus appears that the appearance of a strong absorption at ~300 nm is a consequence of distortion of the chromophore into a twisted 12-s-cis conformation. The data also suggest that 9-*cis*,11-*cis*,13-*cis*-retinal (**2a**) exists predominantly in a twisted 12-s-cis conformation.

This paper further defines the scope of the vinylallene method for synthesizing 11-*cis*-retinoids. Apparently, the application of this approach to 9,10-allenes results in stereospecific production of 11-cis isomers, but there is little control of the stereochemistry of the lateral double bonds (Δ^9 and Δ^{13}) and the 9-cis,11-cis isomers are not stable to the thermal conditions. Future research will be directed toward addressing these problems. Despite these shortcomings, the method still allows rapid access to certain of the hindered 11-*cis*-retinoid analogues in sufficient quantities for further study. Recent reports[15,16] ascribing high activity in the chemoprophylaxis of epithelial cancer to retinoid analogues possessing 12-s-cis topologies make **3–5** attractive candidates for related biological evaluation.

Acknowledgment. The National Institutes of Health (USPHS Grant EY-02452 and NCI Contract CP-05715) provided financial support for this project. We also acknowledge the National Science Foundation Midwest Center for Mass Spectrometry for mass spectra, the Southern California Regional NMR Facility (supported by NSF Grant No. CHE79-16324) for 500-MHz spectra, and BASF (Ludwigshafen) for chemicals.

Registry No. 3a, 83043-75-8; **3b**, 83043-76-9; **4a**, 83043-77-0; **4b**, 83043-78-1; **5a**, 83043-79-2; **5b**, 83043-80-5; **7a**, 83043-81-6; **7b**, 83043-82-7; **8**, 74723-00-5; **9b**, 83043-83-8; **9d**, 83043-86-1; **10a**, 38127-47-8; **10b**, 83043-84-9; **11**, 83060-55-3; **12**, 83043-85-0.

Supplementary Material Available: Spectral data for **7b**, **3ab**, **4ab**, **5ab**, and **11** (2 pages). Ordering information is given on any current masthead page.

(11) All new compounds were characterized by ^{1}H and ^{13}C NMR, IR, and low- and high-resolution mass spectra and by UV as appropriate (see supplementary material section). The UV data (95% EtOH) for the retinals **3a–5a** and retinols **3b–5b** are as follows: (**3a**) λ_{max} 358 nm (sh, ϵ 9500), 288 nm (ϵ 19 300), 251 nm (ϵ 19 500), 235 nm (sh, ϵ 17 600); (**4a**) λ_{max} 357 nm (sh, ϵ 4900), 300 nm (ϵ 27 200), 236 nm (ϵ 20 300); (**5a**) λ_{max} 362 nm (sh, ϵ 3200), 299 nm (ϵ 23 000), 233 nm (ϵ 18 800); (**3b**) λ_{max} 308.5 nm (ϵ 19 700), 230 nm (ϵ 9700); (**4b**) λ_{max} 305 nm (ϵ 28 800), 230 nm (ϵ 11 000); (**5b**) λ_{max} 303 nm (ϵ 24 400), 223 nm (ϵ 9400).

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Electrocyclization of 1-Allenyldienes: Novel Synthesis of Drimatrienes and Related *trans*-Decalins

Wolfgang Reischl and William H. Okamura*

Department of Chemistry
University of California, Riverside
Riverside, California 92521

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Vinylallenes of the type **1** are useful intermediates for preparing polyenes such as vitamin D[1] and 11-*cis*-retinoids,[2] wherein a key step is a $C_6 \rightarrow C_2$ hydrogen migration, a thermal suprafacial [1,5]sigmatropic shift.[3,4] In order to further define the scope of this allene approach in organic synthesis, we considered the diene–allene[5] of the type **2**; it was initially assumed that it would undergo an exceptionally rapid $C_8 \rightarrow C_2$ antarafacial [1,7]sig-

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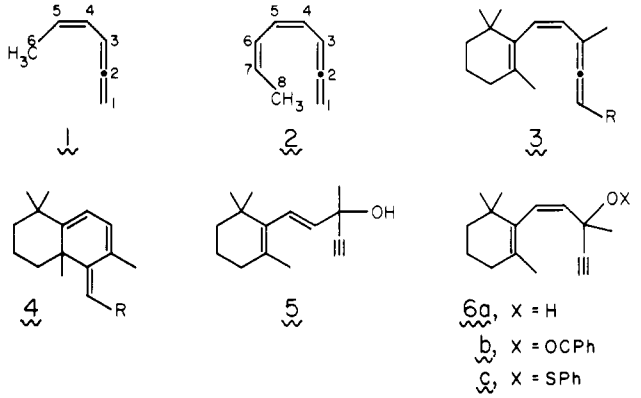
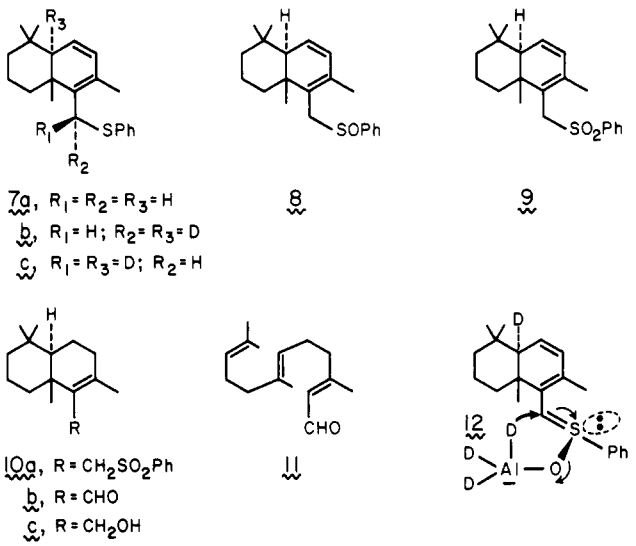
matropic shift.[3] It is the purpose of this communication to describe attempts to synthesize **3**, to reveal that the putative **3** undergoes spontaneous six-electron electrocyclization (and not the anticipated [1,7]sigmatropic shift) to the drimatriene **4**, and finally, to report on some of the novel reactions that one of the drimatrienes (**4**, R = SOPh) undergoes.



Triplet-sensitized photoisomerization[6] of **5**[2a] (2′-acetonaphthone, N_2, benzene, Pyrex, 450-W Hanovia medium-pressure lamp, 16 h) afforded 7-*cis*-propargyl alcohol **6a** (94% distilled yield, 16 g scale),[7] which was transformed to benzoate **6b** (*n*-BuLi, THF and then PhCOCl; viscous liquid, ca. quantitative).[8] Treatment of **6b** with higher order mixed cuprate $R_2Cu(CN)Li_2$[9] (1:2 mole ratio) in ether (−78 °C to room temperature) afforded **4** (R = *n*-Bu, 77%; R = *t*-Bu, 79%; R = Ph, 60%), which presumably results from an initial S_N2' type substitution[1,2] to afford **3** followed by the sterically more accessible of the two possible modes of disrotatory electrocyclization.[10] In order to prepare a derivative of **4** with a more useful functional group R, we reacted the parent alcohol **6a** directly with PhSCl and triethylamine (1:1:2, CH_2Cl_2, −78 °C to room temperature),[11] which nicely afforded an ~80% yield of a separable ~3:2 diastereomeric mixture of triene sulfoxide **4** (R = SOPh). The latter is presumably formed via the following sequence: **6a** → **6c**; [2,3]sigmatropic shift, **6c** → **3** (R = SOPh); electrocyclization **3** → **4** (R = SOPh).

Reaction of **4** (R = SOPh) with a 12-fold excess of $LiAlH_4$[12] (ether, −78 °C to room temperature) afforded a 90% yield of the *trans*-decalin **7a**. The trans ring junction was established as follows. Oxidation (MCPBA, CH_2Cl_2; 75%) of **7a** afforded sulfoxide **8**,[13] which was further oxidized (oxone, CH_3OH–H_2O; 60%)[14] to sulfone **9**. The latter could be prepared more directly by direct oxone oxidation (60% yield) of sulfide **7a**. Catalytic hydrogenation (H_2, Pd/C, ethanol) of **9** afforded monoene **10a**, which was converted to the aldehyde **10b** (1.2 equiv of LDA, THF; 5.0 equiv of MoOPh; 40%).[15] Reduction ($LiAlH_4$, ether, 0 °C, 75%) of **10b** afforded β-bicyclofarnesol **10c**, which proved identical (mp, mixed mp, ^1H NMR, LC) with the material prepared from farnesal **11**.[16]



That lithium aluminum hydride reduction of diastereomeric sulfoxides **4** (R = SOPh) produces only **7a** is most unusual. Accordingly, labeling studies have been carried out to gain some insight into the course of this reduction. Reaction with $LiAlD_4$ followed by H_2O quench of either diastereomer of **4** (R = SOPh) affords **7b**/**c** containing two deuterium atoms; the complementary experiment using $LiAlH_4$ followed by D_2O quench affords only undeuterated **7a**. Thus, this unusual 1,6-reduction of the triene moiety results directly from hydride reagent. More significantly, the major, crystalline diastereomer **4** (R = SOPh) produces a >9:1 ratio of **7b**:**7c** (or vice versa) while its minor, liquid diastereomer affords an opposite >9:1 ratio of **7c**:**7b** (or vice versa). The reaction pathway is therefore hypothesized as an initial attack[17] of deuteride (hydride) at the bridgehead carbon of **4** (R = SOPh) to afford the species **12** (shown only for one of four stereoisomers), which establishes the trans ring junction. This is followed by intramolecular sulfoxide (chiral) directed deuteride transfer to produce **7c** as shown for **12**.

The net transformation **6** → [**3**] → **4** has the potential for broad synthetic applications, including natural products syntheses. Besides the obvious possibility of applying the scheme to other ring sizes and substitution patterns, both steps of the sequence ([2,3]sigmatropic shift; disrotatory electrocyclization) have been established to be stereospecific in simpler systems. This implies that is should be possible to transfer the center of chirality in **6** via the axis of chirality in **3** to a center of chirality at the bridgehead carbon in **4**. This tandem center → axis → center chirality transfer process[18] would be novel as well as useful, and we are actively pursuing efforts directed toward demonstrating this putative process by using optically active variants of **6**.

Acknowledgment. We gratefully acknowledge financial support from the National Institutes of Health (Grant No. EY-02452 and NCI Contract No. CP-05715). We also express our gratitude to BASF (Ludwigshafen) for chemicals, the NSF Midwest Center

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for Mass Spectrometry for mass spectra and the Southern California Regional NMR Facility for the 500-MHz NMR spectra (NSF Grant No. CHE79-16324). W.R. is a recipient of a Fulbright Fellowship. We also acknowledge Beverly Scher, who under an NSF-URP grant the summer of 1980 carried out several initial experiments on this project.

Registry No. (*Z*)-**3** (R = Bu), 83043-56-5; (*Z*)-**3** (R = *t*-Bu), 83043-68-9; (*Z*)-**3** (R = Ph), 83043-69-0; (*E*)-(*R**,*R**)-**4** (R = SOPh), 83043-57-6; (E)-(*R**,*S**)-**4** (R = SOPh), 83043-64-5; **4** (R = Bu), 83043-65-6; **4** (R = *t*-Bu), 83043-66-7; **4** (R = Ph), 83043-67-8; (*E*)-**5**, 17974-59-3; (*Z*)-**6a**, 83060-53-1; (*Z*)-**6b**, 83043-58-7; **7a**, 83043-59-8; **8**, 83043-60-1; **9**, 83043-61-2; **10a**, 83043-62-3; **10b**, 83113-64-8; **10c**, 83043-63-4.

Supplementary Material Available: Selected spectral data (^{1}H NMR, ^{13}C NMR, IR, and/or UV) for **4** (R = SOPh, *n*-Bu, *t*-Bu, Ph, H), **6a**, **6b**, **7a**, **7b**, **7c**, **8**, **9**, **10a**, **10b**, and **10c** (6 pages). Ordering information is given on any current masthead page.

Chlorophyll *a* Sensitized Trans-Cis Photoisomerization of *all-trans*-β-Carotene

Niels-Henrik Jensen,* Anne B. Nielsen, and Robert Wilbrandt

Chemistry Department, Risø National Laboratory DK-4000 Roskilde, Denmark

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Carotenoids are widely distributed in nature,[1,2] and protection of the various organisms against photodestruction seems to be a general function of the carotenoids.[3,4] In photosynthetic organisms, the carotenoids also serve as accessory pigments in the light-harvesting process.[5-7] The excited triplet states of carotenoids are important intermediates in the protective reactions, and consequently the triplet states of carotenoids have been the subject of numerous investigations. Recently the excited triplet states of *all-trans*-β-carotene and other polyenes have been studied by time-resolved resonance Raman spectroscopy by us[8-11] and by Dallinger et al.[12,13] Although the experimental results of the two groups are similar, the interpretations suggested are different, implying either substantial twisting around double bonds[8,9] or essentially no changes in geometry[13] upon electronic excitation. Theoretical calculations[14-16] and extrapolation of the results obtained with shorter polyenes[17] support the former suggestion, while the apparent stability of *all-trans*-β-carotene toward trans-cis isomerization under conditions where the triplet state is produced[13,18-25] supports the latter. Prompted by these conflicting reports and by the possible importance of *cis*-carotenoids in photosynthetic organisms,[26-29] we have initiated a study of the triplet state chemistry of *all-trans*-β-carotene (all-trans) and related compounds.

Illumination with red light (λ >610 nm, 25-mm H_2O filter, 89 mW/cm^2) of a 10^{-3} M solution of all-trans[30] in Ar-saturated

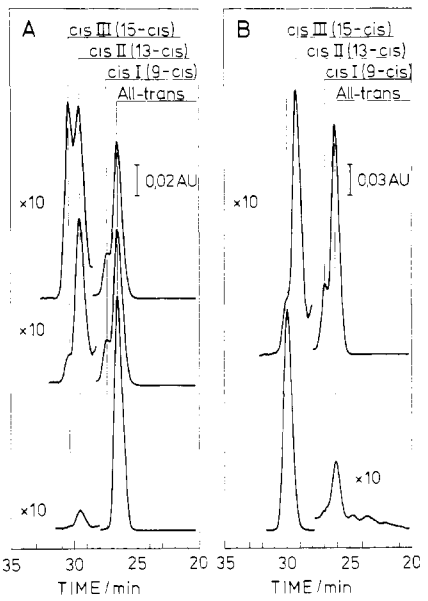

Figure 1. Chromatograms of β-carotene before and after Chl *a* sensitized photoisomerization. The Ar-saturated solutions all contained 2×10^{-5} M Chl *a*. Analysis wavelength 440 nm, other conditions specified in text. (A) Lower trace, 10^{-3} M all-trans before illumination; middle trace, the same solution after illumination for 15 min with λ >610 nm; upper trace, illuminated solution mixed with authentic 15-*cis*-β-carotene. Samples diluted ten times with acetone before HPLC. (B) Lower trace, 10^{-3} M 15-cis before illumination; upper trace, 10^{-3} M 15-cis after illumination for 15 min with λ >610 nm. Samples diluted five times with acetone before HPLC.

Table I. Spectral Data of Photoisomers[a]

	absorbance max, nm	$\epsilon_{max}/\epsilon_{341}$
all-trans	482, *455*, ~434 sh	20.69 ± 0.32
cis I (9-cis)	476, *450*, ~430 sh, 341	9.40 ± 0.58
cis II (13-cis)	474, *448*, ~430 sh, 341	2.16 ± 0.05
cis III (15-cis)	475, *452*, ~430 sh, 341	1.62 ± 0.18
15-cis[b]	475, *452*, ~430 sh, 341	1.65

[a] Solvent, 88% acetone/12% H_2O; maximum is in italics; sh, shoulder. Spectra were taken in a flow-cell after HPLC. [b] Sample of authentic 15,15′-*cis*-β-carotene.

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