natural sources[23] except for optical activity and melting point. Simple treatment of **23** with fluoride ion yielded (±)-verrucarol [mp 165.5–167 °C (ether–chloroform)],[28] again identical with the natural material except for optical activity and melting point.[29]

Presently work is underway to synthesize 11-epiverrucarol from the diol **14**. We are also hoping to convert the triene **20b** to some of the C-3,C-4 diols such as anguidine. This highly efficient synthesis of the trichothecane skeleton and its C-11 epimer should provide some intriguing analogues, not readily available from natural sources, in quantities suitable for biological testing.

Acknowledgment. We express our warm appreciation to the National Cancer Institute for their generous support. We are grateful to Dr. Ken Haller for collaborating in the X-ray determination of a critical intermediate and Professor Christoph Tamm for providing a generous authentic sample of the natural products.

Registry No. (±)-**2**, 80514-49-4; **4b**, 58274-64-9; **5**, 82891-01-8; **6**, 7523-44-6; (±)-**7**, 82891-02-9; (±)-**8**, 82902-13-4; (±)-**9**, 82891-03-0; (±)-**10**, 82891-04-1; (±)-**11**, 82891-05-2; (±)-**12**, 82891-06-3; (±)-**13a**, 82891-07-4; (±)-**14**, 82916-70-9; (±)-**15**, 82891-08-5; (±)-**16**, 82916-71-0; (±)-**17**, 82891-09-6; (±)-**18**, 82891-10-9; (±)-**19a**, 82891-11-0; (±)-**19b**, 82891-12-1; (±)-**20a**, 82891-13-2; (±)-**20b**, 82891-14-3; (±)-**21a**, 82891-15-4; (±)-**21b**, 82891-16-5; (±)-**22**, 82891-17-6; (±)-**23**, 82891-18-7; 2-methyl-1,3-cyclopentanedione, 765-69-5; cesium propionate, 38869-24-8.

Supplementary Material Available: Full spectral data for compounds **9**, **11**, **13a**, **16**, **19a**, and **23** (2 pages). Ordering information is given on any current masthead page.

(27) Peracid oxidation (mCPBA, −26 °C) exhibited moderate chemoselectivity (66% at 60% conversion). Both the undesired 9,10-monoepoxide and the 9,10,12,13-diepoxide could be detected in the ^{1}H NMR (270 MHz) spectrum. When $VO(acac)_2$ was used as the metal catalyst, decomposition as well as the desired oxidation accompanied the disappearance of starting material.

(28) Our melting point for racemic verrucarol is some 6 °C higher than that reported by Schlessinger and Nugent (ref 4c). Since these authors were the first to prepare the racemate, we are somewhat puzzled by the literature citation given by these authors for racemic verrucarol. To our knowledge all literature melting points are for the optically pure compound (mp 155–156 °C, ref 29).

(29) Gutzwiller, J.; Mauli, R.; Sigg, H. P.; Tamm, Ch. *Helv. Chim. Acta* **1964**, *47*, 2234.

Macrocyclization via an Isomerization Reaction at High Concentrations Promoted by Palladium Templates

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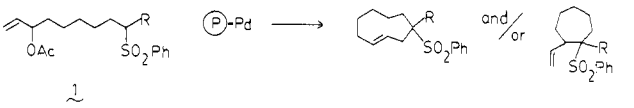
The ability to form medium and macrocyclic rings has normally relied upon high dilution to ensure intramolecular vs. intermolecular reactions.[1] The inefficiency associated with large volumes of solvent, which can be somewhat ameliorated by the use of slow addition techniques, encourages exploration of methodology that avoids high dilution. The principle of "pseudodilution" within cross-linked polymers,[2] which has been so successfully employed in peptide synthesis, had not been successfully applied to macrocyclization (except for cyclic peptides[3]) at the time we initiated our work.[4] Most recently, the use of this approach for macrolactonization has been reported; however, substrate concentrations were still <0.003 M.[5] We report an approach to forming medium and large rings via C–C bond formation that permits utilization of 0.1–0.5 M concentrations of substrates in simple bulk solution.

Polymer-supported transition-metal-mediated macrocyclization[6] offers a simplistic solution to this problem at first glance. With the catalyst anchored on an insoluble support,[7] a pseudodilution effect arises from the low concentration of the "active sites" in a phase apart from that containing the substrate. Thus, the substrate must diffuse to the catalytic site before it becomes activated for cyclization. The combinatorial effect of having relatively few catalytic sites and even fewer occupied at the same time should ensure an intramolecular reaction. Use of the sodium salt of **1**, R = CO_2CH_3 or $PhSO_2$ with a polystyrene polymeric



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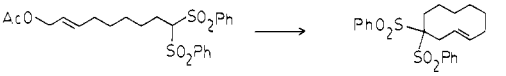
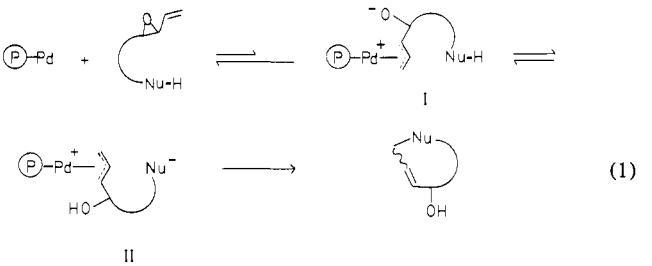
catalyst that bore both benzo-12-crown-4[8] and phosphine ligands binding palladium(0) as well as simple macroreticular polystyrene polymeric supports bearing palladium(0) ligated with phosphines led to both seven- and nine-membered ring products in low yields with varying amounts of starting material and/or elimination product.[9] The best result obtained involved the cyclization of **2**, which gave only 4,4-bis(benzenesulfonyl)-*E*-cyclononene in



2 3

20% yield with 76% recovery of starting material (83% yield based upon recovered starting material).

Perceiving that problem as related to the use of salts whose diffusion to the catalytically active sites on these lipophilic polymers was unfavorable, we sought a neutral cyclization precursor that upon binding to the active site generates both the nucleophilic and electrophilic partners required in the cyclization. Vinyl epoxides[10,11] as represented by **4** and **5** (Scheme I) represent ideal choices. The chemoselectivity in the final step of their synthesis, i.e., the alkylation of the bromo vinyl epoxides, should be noted. Thus, the vinyl epoxide is not a reactive electrophile in aprotic solvents in the absence of palladium catalysts. Equation 1 rep-



(1) For a recent critical evaluation of macrolactonization methods see: Galli, C.; Mandolini, L. *J. Chem. Soc., Chem. Commun.* **1982**, 251. For reviews on macrolides see: Nicolaou, K. C. *Tetrahedron* **1977**, *33*, 683. Masamune, S.; Bates, G. S.; Corcoran, J. W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 585. Back, T. G. *Tetrahedron* **1977**, *33*, 3041. Newkome, G. R.; Sauer, J. D.; Roper, J. M.; Hager, D. C. *Chem. Rev.* **1977**, *77*, 513.

(2) Mazur, S.; Jayalekshmy, P. *J. Am. Chem. Soc.* **1979**, *101*, 677. Rebek, J., Jr., Trend, J. E. *Ibid.* **1979**, *101*, 737. Chang, Y. H.; Ford, W. T. *J. Org. Chem.* **1981**, *46*, 5364 and references therein.

(3) Fridkin, M.; Patchornik, A.; Katchalski, E. *Isr. J. Chem.* **1965**, *3*, 69; *J. Am. Chem. Soc.* **1965**, *87*, 4646.

(4) Crowley, J. I.; Rapoport, H. *J. Org. Chem.* **1980**, *45*, 3215; *Acc. Chem. Res.* **1976**, *9*, 135.

(5) Regen, S. L.; Kumura, Y. *J. Am. Chem. Soc.* **1982**, *104*, 2064.

(6) For palladium-catalyzed macrocyclization see: Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4743 and earlier references therein. Kitagawa, Y.; Itoh, A.; Hashimoto, S.; Yamamoto, H.; Nozaki, H. *Ibid.* **1977**, *99*, 3864.

(7) For polystyrene-supported palladium catalysts see: Trost, B. M.; Keinan, E. *J. Am. Chem. Soc.* **1978**, *100*, 7779. Pittman, C. U., Jr.; Ng, Q. *J. Organomet. Chem.* **1978**, *153*, 85. Terasawa, M.; Kaneda, K.; Imanaka, T.; Teranishi, S. *Ibid.* **1978**, *162*, 403.

(8) Cf.: Warshawsky, A.; Kalir, R.; Deshe, A.; Berkovitz, H.; Patchornik, A. *J. Am. Chem. Soc.* **1979**, *101*, 4249.

(9) Keinan, E., unpublished observations in these laboratories.

(10) Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969.

(11) For isomerizations of vinyl epoxides see: Suzuki, M.; Oda, Y. Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623.

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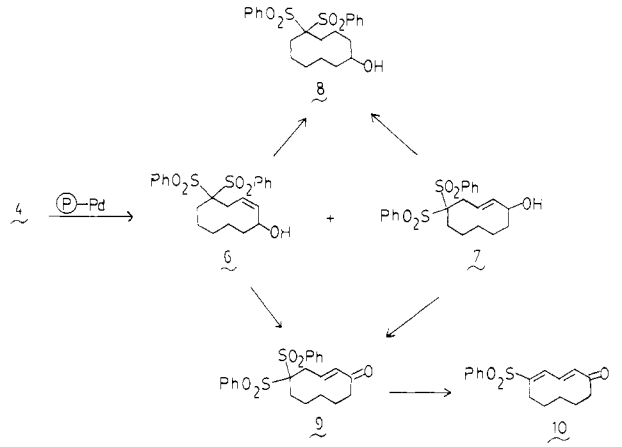
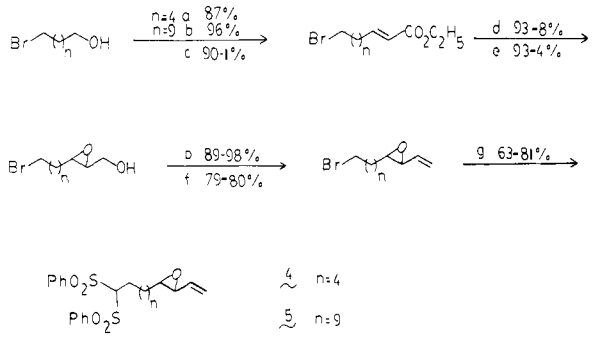
resents the envisioned path in which the isolation of I and II should promote an intramolecular reaction. The fact that II is formed as an ion pair (necessitated by the proximity required for proton transfer in I) in a lipophilic medium (the polymer) inhibits charge separation and consequently should favor collapse to the macrocycle.

Exposure of 0.1–0.5 M solution of **4** in refluxing THF to ap-



proximately 5 mol % of a polymerically bound palladium(0) catalyst (a low cross-linked polystyrene support containing 5.2 phosphines/palladium)[12] led to production of two isomeric products in a 2:1 ratio in a yield of 71%, which is an average over 10 runs. That they were isomeric at the double bond was suggested by the 14.0-Hz coupling for the vinyl proton of the major isomer **6** (δ 5.58 and 5.46), the 17.8-Hz coupling for the minor isomer **7** (δ 5.98 and 5.57) and their hydrogenation (**6**, 3 atm of H_2, 10% PtO_2, C_2H_5OH, HOAc; **7**, 1 atm of H_2, 10% Pd/C, C_2H_5OH) to the identical alcohol **8**, mp 218–219 °C. Their monomeric nature was supported by the ^{13}C spectra, which showed 12 distinct absorptions for the 14 different carbons of **6** and **7** and their further transformation products **9**[13] and **10**. Oxidation of both **6** and **7** [Me_2SO, $(COCl)_2$, $(C_2H_5)_3N$, CH_2Cl_2, 96%] was accompanied by double-bond isomerization to a single pure enone **9**,[13] mp 189–191 °C, which has tentatively been assigned the *E* stereochemistry.[14] The ^{13}C NMR spectrum of **9** resolves each carbon.[13] While **6**, **7**, and **9** only show fragmentation in the mass spectrum, the dienone **10**, which results in 86% yield by subjecting **9** to DBU in CH_2Cl_2, shows a clear molecular ion at *m/e* 290.0978 (calcd 290.0956). No higher mass peaks were detected.

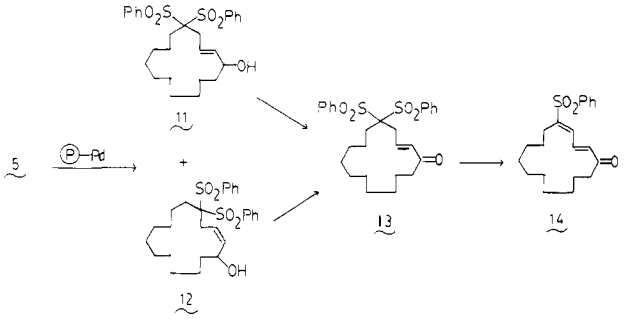
Scheme I. Synthesis of Cyclization Precursors



[a] PCC, NaOAc, CH_2Cl_2. [b] $(COCl)_2$, Me_2SO, $(C_2H_5)_3N$, CH_2Cl_2, −78 °C. [c] $(C_2H_5O)_2P(O)CH_2CO_2C_2H_5$, NaH, THF, 0 °C. [d] Dibal-H, $PhCH_3$, 0 °C. [e] MCPBA, NaOAc, CH_2Cl_2, 0 °C. [f] $Ph_3P^+CH_3Br^-$, $K^+O^-t\text{-}C_4H_9$, THF, −78 °C. [g] $(PhSO_2)_2CH_2$, NaH, DMF, room temperature.

That the polymeric catalyst was necessary for successful monomeric cyclization was illustrated by subjecting a 0.1 M solution of **4** to 5 mol % $(Ph_3P)_4Pd$ in the presence of dppe, in which case only oligomeric products were obtained. As expected, these products do reveal fragmentation peaks in the mass spectrum at *m/e* substantially above those corresponding to monomer.

To demonstrate the feasibility of this approach to large as well as medium size rings, we subjected **5** to the identical conditions



to give a 4:1 mixture of two isomers in 66% yield, which is an average over 10 runs. The major isomer was assigned the *E*-olefin stereochemistry based upon J = 17.9 Hz for the vinyl protons (δ 5.60 and 6.10), whereas the minor isomer showed J = 14.0 Hz for these protons (δ 5.89 and 5.65) and was assigned the *Z* stereochemistry. While the ^{13}C NMR spectra of **11** and **12** did not fully resolve all the carbons, the corresponding ketone **13**,[13] mp 172–174 °C, which derives from **11** or **12** by a Moffatt-type oxidation as before in 92% yield, does display 18 of the 19 carbons (one redundancy) in the ^{13}C NMR spectrum.[13] Further, the elimination product **14**, which forms in 90% yield, displays a clean molecular ion at *m/e* 360.1759 (calcd 360.1758) with no higher mass peaks—a further confirmation of the monomeric nature of the product.

These cyclizations show a remarkable concentration dependence. Performing the reaction at 0.01 or 1 M in substrate led mainly to recovered starting material even after 12 h at reflux (normal reaction time is 2–3 h). While a very slow reaction at low concentrations is understandable, the sluggishness at higher concentrations is more perplexing. The high viscosity of the medium at 1 M apparently is responsible since dilution to 0.1–0.5 M initiates cyclization. Temperature also appears to be critical. Clean cyclizations occur at 65 °C (bath temperature 78 °C), whereas lower temperatures lead to other products. Best results are achieved if the solution of the substrate is added to a preheated suspension of the catalyst. On the other hand, solvent is less critical. Equivalent results were obtained in toluene with only the *E*:*Z* ratio of products changing slightly.

This mode of cyclization provides an unusually facile entry into both a medium- and a large-size ring without the need to resort to high dilution. The fact that the cyclization is simply an

(12) A Rohm and Haas Amberlite XE-305 A resin was brominated and phosphinylated [Schwartz, R. H.; San Filippo, J., Jr *J. Org. Chem.* **1979**, *44*, 2705] and loaded by exchanging with $(Ph_3P)_4Pd$ in PhH. Anal. P, 5.75; Pd, 3.76.

(13) **4**: IR ($CHCl_3$): 1650, 1590, 1335, 1315, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93 (m, 4 H), 7.68 (7, 2 H), 7.56 (m, 4 H), 5.51 (ddd, J = 17.1, 9.7, 7.3 Hz, 1 H), 5.43 (dd, J = 17.1, 1.8 Hz, 1 H), 5.23 (dd, J = 9.7, 1.8 Hz, 1 H), 4.36 (t, J = 5.5 Hz, 1 H), 3.06 (dd, J = 7.3, 2.2 Hz, 1 H), 2.80 (m, 1 H), 2.15 (m, 2 H), 1.53–1.15 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 137.7, 135.5, 134.2, 129.28 128.8, 118.6, 83.4, 60.0, 58.3, 31.5, 28.6, 27.8, 25.6, 25.4. **5**: IR ($CHCl_3$) 1650, 1590, 1335, 1315, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93 (m, 4 H), 7.68 (m, 2 H), 7.56 (m, 4 H), 5.54 (ddd, J = 16.1, 9.9, 6.9 Hz, 1 H), 5.43 (dd, J = 16.1, 1.8 Hz, 1 H), 5.23 (dd, J = 9.9, 1.8 Hz, 1 H), 4.34 (t, J = 5.5 Hz, 1 H), 3.06 (dd, J = 6.9, 2.2 Hz 1 H), 2.80 (m, 1 H), 2.15 (m, 2 H), 1.53–1.15 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 138.0, 135.9, 134.4, 129.5, 129.0, 118.6, 83.9, 60.4, 58.6, 31.9, 29.3, 28.9, 28.1, 25.8, 25.7. **9**: IR ($CHCl_3$) 1670, 1630, 1310, 1140 cm^{-1}; ^1H NMR ($CDCl_3$), δ 8.03 (m, 4 H), 7.71 (m, 2 H), 7.59 (m, 2 H), 6.91 (dt, J = 15.4, 8.1 Hz, 1 H), 6.10 (d, J = 15.4 Hz, 1 H), 3.10 (d, J = 7.3 Hz, 2 H), 2.60 (t, J = 4.8 Hz, 2 H), 2.07 (m, 2 H), 1.59 (m, 4 H), 1.39 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 203.5, 138.3, 136.3, 136.1, 134.6, 131.1, 128.6, 92.2, 38.9, 35.7, 30.5, 29.5, 23.5, 19.3. Anal. for $C_{22}H_{26}O_5S_2$: C, H. **13** IR ($CHCl_3$) 1670, 1630, 1330, 1310, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.02 (m, 4 H), 7.70 (m, 2 H), 7.59 (m, 4 H), 7.05 (dt, J = 15.8, 7.0 Hz, 1 H), 6.22 (d, J = 15.8 Hz, 1 H), 3.17 (d, J = 5.9 Hz, 2 H), 2.52 (t, J = 6.2 Hz, 2 H), 2.15 (m, 2 H), 1.62 (m), 1.27 (m); ^{13}C NMR ($CDCl_3$) δ 200.7, 138.7, 136.5, 134.9, 134.7, 131.2, 128.7, 91.0, 39.9, 31.3, 28.3, 27.4, 26.5, 26.2, 26.0 (2 C), 25.1, 24.4, 21.2. Anal. for $C_{27}H_{34}O_5S_2$: C, H.

(14) For cyclodec-2-en-1-one, the *E* isomer shows J = 16.3, Hz and the *Z* isomer J = 12.0 Hz. Whitham, G. H.; Zaidlewicz, M. *J. Chem. Soc., Perkin Trans 1* **1972**, 1509.

isomerization makes such a process very attractive. It is noteworthy that although the proton transfer in the conversion of I to II (eq 1) involves a 1,8 and a 1,13 shift, respectively, no competition of the simple vinyl epoxide isomerization to enones occurs.[11] This type of cyclization holds promise of being a general solution to normally unfavorable ring sizes. Furthermore, the juxtaposition of functionality in the specific cases chosen offers an opportunity for further elaboration toward natural products such as the polyene macrolides.[15] A simple illustration from **13** to muscone can be envisioned by conjugate addition of lithium dimethylcuprate followed by reductive desulfonylation.[16]

Acknowledgment. We thank the National Science Foundation and the General Medical Sciences Institute of the National Institutes of Health for their generous support of our programs. We are grateful to Rohm and Haas for a generous gift of the polystyrene resin and Englehardt Industries and Johnson Matthey for a generous supply of palladium chloride.

Registry No. 1 (R = CO_2CH_3) Na, 82902-78-1; **1** (R = $PhSO_2$) Na, 82917-43-9; **2**, 82902-79-2; **3**, 82902-80-5; **4**, 82902-81-6; **5**, 82917-44-0; **6**, 82902-82-7; **7**, 82902-83-8; **8**, 82902-84-9; **9**, 82902-85-0; **10**, 82902-86-1; **11**, 82902-87-2; **12**, 82902-88-3; **13**, 82902-89-4; **14**, 82902-90-7; ethyl 8-bromo-2-octenoate, 82902-91-8; ethyl 13-bromo-2-tridecenoate, 82902-92-9; 8-bromo-2,3-epoxyoctanol, 82902-93-0; 13-bromo-2,3-epoxytridecanol, 82902-94-1; 2-(5-bromopentyl)-3-ethenyloxirane, 82902-95-2; 2-(10-bromodecyl)-3-ethenyloxirane, 82902-96-3; 6-bromohexanol, 4286-55-9; 11-bromoundecanol, 1611-56-9; methyl 1-phenylsulfonyl-3-cyclononene-1-carboxylate, 70255-45-7; 4,4-diphenylsulfonylcyclononene, 70255-47-9; methyl 1-phenylsulfonyl-2-ethenylcycloheptanecarboxylate, 70255-46-8; 1,1-diphenylsulfonyl-2-ethenylcycloheptane, 70255-48-0; $(Ph_3P)_4Pd$, 14221-01-3; dppe, 1663-45-2.

(15) Oroshnik, W.; Mebane, A. D. *Fortsch. Chem. Org. Naturst.* **1963**, *21*, 17. Hamilton-Miller, J. M. T. *Bacteriol. Rev.* **1973**, *37*, 166.
(16) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem.* **1980**, *102*, 4730. Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

12-s-Cis-Locked Retinoids (Vitamin A): Synthesis and Novel Spectral Properties

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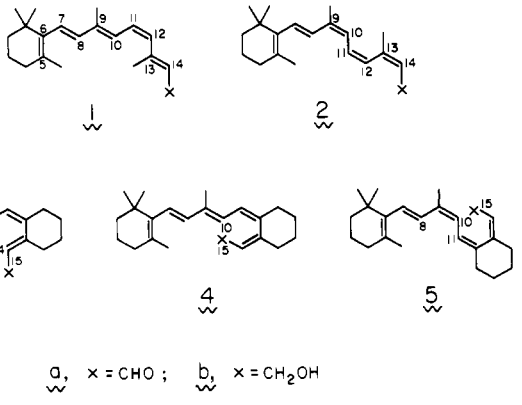
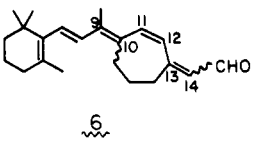
The chromophoric group of the visual pigment rhodopsin, 11-*cis*-retinal (**1a**),[1] is believed to exist in solution as an equilibrium



1a, X = CHO; **b**, X = CH_2OH

mixture of twisted 12-s-cis and 12-s-trans conformers.[2] The observation that **1a** and the corresponding alcohol **1b** exhibit UV maxima at 377 and 319 nm,[3] respectively, is indicative of a highly distorted chromophore for each.[3] We recently made the unusual observation that the more hindered 9-*cis*,11-*cis*,13-*cis*-retinal (**2a**) exhibits its main maximum (302 nm) to the blue of the corresponding alcohol **2b** (306 nm).[4a] The ^1H NMR data indicated that a high degree of distortion exists about the C(12)–C(13) single bond.[4a] In order to further evaluate this effect, this communication describes the synthesis and spectral properties of highly twisted 12-s-cis-locked retinal analogues possessing 11-cis (**3a**), 11-cis,13-cis (**4a**), and 9-cis,11-cis,13-cis (**5a**) geometries. This study nicely complements that of Nakanishi and co-workers on twisted 12-s-trans-locked retinals **6**, which exhibit relatively normal



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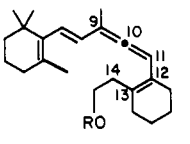
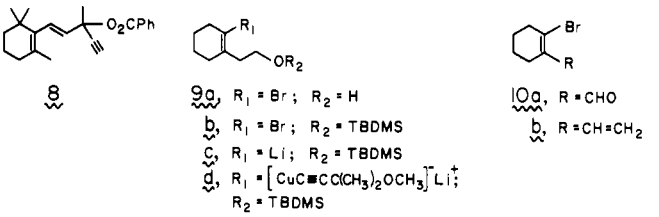
(TBDMS = t-$BuMe_2Si$)



7a, R = TBDMS
b, R = H

electronic spectra (λ_{max} >350 nm) for both the 11-cis and 9-cis,11-cis,13-cis geometric isomers.[5] The synthetic route used for preparing **3**–**5** entails the [1,5] sigmatropic hydrogen shift of the vinylallene **7b** as a key step, a process specific for producing 11-*cis*-retinoids.[4] This process should have also produced a 9-cis,11-cis isomer, but the latter apparently undergoes further previously unrecognized[4a] pericyclic transformations. This study therefore also provides further insight into the stereochemical course of vinylallene rearrangements.

The vinylallene **7a** was obtained by the coupling of the propargyl benzoate **8** and the vinyl cuprate **9d**,[4,6] which was prepared as



8

9a, R_1 = Br; R_2 = H
b, R_1 = Br; R_2 = TBDMS
c, R_1 = Li; R_2 = TBDMS
d, R_1 = $[CuC{\equiv}CC(CH_3)_2OCH_3]^-Li^+$; R_2 = TBDMS

10a, R = CHO
b, R = $CH{=}CH_2$

follows. Reaction of **10a** (prepared in 52% yield from cyclohexanone)[7] under Wittig conditions (ether, Ph_3PCH_3Br, *n*-BuLi; 54%) gave the bromodiene **10b**. Hydroboration–oxidation (THF, 9-BBN; H_2O_2, NaOH, H_2O–CH_3OH; 85%)[8] followed by protection (TBDMSCl, imidazole, DMF; 84%)[9] afforded the bromosilyl ether **9b**. Lithiation (2.1 equiv of *t*-BuLi, ether, −78 °C, 4 h) of **9b** followed by reaction with $CuC{\equiv}C{-}C(CH_3)_2OCH_3$[10] afforded the mixed cuprate **9d**, which was reacted with **8** to afford silyl ether **7a**. Deprotection ($(n\text{-}Bu)_4NF$, THF, room temperature, 4.5 h)[9] of **7a** followed by high-pressure liquid chromatography (HPLC) (15% ethyl acetate–skellysolve B) afforded pure vinyl-

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