Careful medium-pressure liquid chromatography [silica gel, CH_2Cl_2, hexane (9:1)], furnished pure analytical samples of **7** and **7a**. Their ^{13}C NMR spectra, as well as the comparison of the IR spectra of their hydrogenation products with those of authentic **9**,[6] served as final structure proofs. Norketone **9** was converted to hirsutene **1** according to an already published procedure.[6]

The described synthesis proves rewarding in the following ways. First, it marks an easy access to the coriolin class of sesquiterpenes by having served as a model study for the production of the more complicated systems. Several approaches to the oxygenated coriolin nucleus are presently being tested in our laboratory. Second, it ascertains the utility of intramolecular carbenoid addition to 1,3-dienes as a new method for internal cyclopentane annulation. Third, it should be borne in mind that the present approach furnishes hirsutene in 37% overall yield[18] from aldehyde **2** (23% from dimedone), without the use of chromatography, in a single step (except in the preparation of analytical samples); this last criterion makes our approach to the coriolin skeleton attractive from a *practical* point of view.

The synthetic studies of oxygenated coriolins and approaches to the tricyclo[6.3.0.0^{4,8}]undecane subunit of retigeranic acid are the points of current interest in our laboratory.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, and the Department of Chemistry at Illinois Institute of Technology for support of this work. Thanks are extended to Professor K. Tatsuta of Keio University, Japan, for providing us with the spectra of hirsutene and norketone. The use of mass spectral facilities and a high-field NMR spectrometer at Indiana University is gratefully appreciated.

Note Added in Proof: After the submission of this manuscript the authors became aware of two very elegant syntheses of hirsutene: one published by A. E. Greene, *Tetrahedron Lett.* **1980**, 3059; the other forthcoming by Little, R. D., et al.

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(18) The entire synthesis was repeated three times to ascertain reproducibility and to obtain sufficient materials for ^{13}C NMR analysis.

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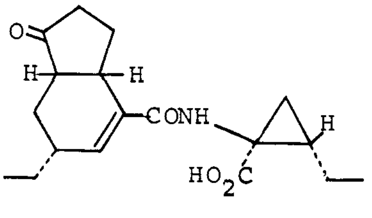
Synthesis of (±)-Coronafacic Acid. Efficient Intramolecular Diels-Alder Reaction of Latent Diene-Dienophile Functionality via Thermal Reaction

Sir:

The structure[1] and stereochemistry[2] of coronatine (**1**), which induces phytotoxic lesions on the leaves of Italian ryegrass and hypertrophic growth of potato tuber tissue, were reported previously. While the synthesis of (±)-coronafacic acid (**2**), the acidic component of coronatine, has been completed,[3] no satisfactory results were obtained for the control of its stereochemistry. In order to solve the problem, we utilized an intramolecular Diels–Alder reaction between *E,E*-diene and enone moieties (a) to produce favorable stereochemistry at C_{3a} and C_6 in **2** (Scheme I). Though a number of intramolecular Diels–Alder reactions have been applied to the synthesis of natural products,[4] difficulties have always arisen in the construction of the labile diene and dienophile moieties. This communication describes a new stereoselective synthesis of (±)-coronafacic acid through thermal reaction of latent diene–dienophile moieties (b) which are masked as an equally, thermally labile cyclobutene (c) and methyl ketone Diels–Alder product (d), readily derived from trivial compounds as shown by retrosynthesis.



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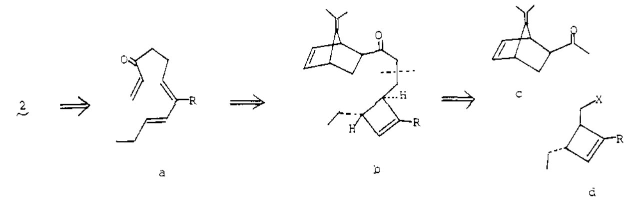
Scheme I



Condensation of the enamine from *n*-butanal and dimethylamine with diethyl maleate, quaternization with *p*-TsOMe, and subsequent elimination yielded known diester **3**[5,6] (63% yield from the enamine) (Scheme II). The stereochemistry of diester **3** was

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(1) Ichihara, A.; Shiraishi, K.; Sato, H.; Sakamura, S.; Nishiyama, K.; Sakai, R.; Furusaki, A.; Matsumoto, T. *J. Am. Chem. Soc.* **1977**, *99*, 636.

(2) (a) Ichihara, A.; Shiraishi, K.; Sakamura, S.; Nishiyama, K.; Sakai, R. *Tetrahedron Lett.* **1977**, 269. (b) Ichihara, A.; Shiraishi, K.; Sakamura, S.; Furusaki, A.; Hashiba, N.; Matsumoto, T. *Ibid.* **1979**, 365.

(3) Ichihara, A.; Kimura, R.; Moriyasu, K.; Sakamura, S. *Tetrahedron Lett.* **1977**, 4331.

(4) (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10; *Ibid.* **1978**, *17*, 793. (b) Kametani, T.; Fukumoto, K. *Heterocycles* **1977**, *8*, 456. (c) Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 6289. (d) Taber, D. F.; Gunn, B. P. *Ibid.* **1979**, *101*, 3992.

(5) Brannock, K. C.; Bell, A. B.; Burpitt, R. D.; Kelly, C. A. *J. Org. Chem.* **1964**, *29*, 801.

(6) Spectral and analytical data for all new compounds are as follows. **3**: IR (neat) 1730, 1620 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 1.00 (3 H, t, $J = 7$ Hz), 1.22 (3 H, t, $J = 7$ Hz), 1.24 (3 H, t, $J = 7$ Hz), 1.62 (2 H, q, $J = 7$ Hz), 2.20 (1 H, dt, $J = 7$, 1.5 Hz), 3.20 (1 H, d, $J = 1.5$ Hz), 4.10 (2 H, q, $J = 7$ Hz), 4.15 (2 H, q, $J = 7$ Hz), 6.85 (1 H, s); M_w calcd for $C_{12}H_{18}O_4$ 226.1205, found 226.1242. 4: IR (neat) 3350, 1010 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 0.90 (3 H, t, $J = 7$ Hz), 1.50 (2 H, q, $J = 7$ Hz), 2.20 (1 H, t, $J = 7$ Hz), 2.60 (1 H, dd, $J = 5$, 9 Hz), 3.48 (1 H, t, $J = 9$ Hz), 3.82 (1 H, dd, $J = 5$, 9 Hz), 4.05 (2 H, s), 6.00 (1 H, s); M_w calcd for $C_8H_{14}O_2$ 142.0992, found 142.0964. Anal. ($C_8H_{14}O_2$) C, H; C calcd, 67.57; found, 68.04. **5**: IR (neat) 3400, 1680 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 1.00 (3 H, t, $J = 7$ Hz), 1.65 (2 H, q, $J = 7$ Hz), 2.50 (1 H, t, $J = 7$ Hz), 2.90 (1 H, m), 3.85 (1 H, dd, $J = 6$, 9 Hz), 7.10 (1 H, d, $J = 2$ Hz), 9.00 (1 H, s); M_w calcd for $C_8H_{12}O_2$ 140.0836, found 140.0826. **6**: IR (neat) 3450, 1080 cm^{-1}; NMR (90 MHz, CCl_4) δ 0.95 (3 H, t, $J = 7$ Hz), 1.55 (2 H, q, $J = 7$ Hz), 2.25 (1 H, t, $J = 7$ Hz), 2.60 (2 H, m), 3.55 (2 H, m), 3.95 (4 H, m), 5.15 (1 H, s), 6.20 (1 H, s); M_w calcd for $C_{10}H_{16}O_3$ 184.1097, found 184.1089. **7**: IR (neat) 2750, 1720, 1090 cm^{-1}; NMR (90 MHz, CCl_4) δ 1.00 (3 H, t, $J = 7$ Hz), 1.60 (2 H, q, $J = 7$ Hz), 2.25 (1 H, t, $J = 7$ Hz), 3.00 (1 H, d, $J = 4.5$ Hz), 3.85 (4 H, s), 5.22 (1 H, s), 6.40 (1 H, s), 9.00 (1 H, d, $J = 4.5$ Hz); M_w calcd for $C_{10}H_{14}O_3$ 182.0942, found 182.0941. **8**: IR (neat) 1710 cm^{-1}; NMR (90 MHz, CCl_4) δ 1.54 (3 H, s), 1.56 (3 H, s), 2.05 (3 H, s), 1.20–2.90 (3 H, m), 3.20 (1 H, m), 3.40 (1 H, m), 6.20 (2 H, m); M_w calcd for $C_{12}H_{16}O$ 176.1201, found 176.1214. **9**: IR (neat) 3450, 1700 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 0.95 (3 H, t, $J = 7$ Hz), 1.60 (6 H, s), 1.40–2.00 (3 H, m), 2.20 (1 H, m), 2.40–2.70 (3 H, m), 2.20 (1 H, m), 3.00 (1 H, m), 3.30 (1 H, m), 3.60 (1 H, m), 3.90 (5 H, m), 5.20 (1 H, m), 6.30 (1 H, m), 6.40 (2 H, m); M_w calcd for $C_{22}H_{30}O_4$ 358.2142, found 358.2140. **10**: IR (neat) 1690, 1670, 1620 cm^{-1}; NMR (90 MHz, CCl_4) δ 1.00 (3 H, t, $J = 7$ Hz), 1.60 (6 H, s), 1.25–2.10 (3 H, m), 2.50 (1 H, m), 3.15 (1 H, d, $J = 8$ Hz), 3.35, 3.45 (each 1 H, m), 4.00 (4 H, m), 6.20 (1 H, d, $J = 16$ Hz), 6.30 (3 H, br s), 6.85 (1 H, dd, $J = 8$, 16 Hz); M_w calcd for $C_{22}H_{28}O_3$ 340.2037, found 340.2026. **11**: IR (neat) 1710, 1090 cm^{-1}; NMR (90 MHz, CCl_4) δ 0.95 (3 H, t, $J = 7$ Hz), 1.55, 1.60 (each 3 H, s), 1.10–2.60 (11 H, m), 3.40, 3.50 (each 1 H, m), 3.90 (4 H, m), 5.20 (1 H, s), 6.15 (1 H, s), 6.25 (2 H, m). Anal. ($C_{22}H_{30}O_3$) C, H. **12**: IR (KBr) 1740 cm^{-1}; NMR (90 MHz, CCl_4) δ 0.95 (3 H, t, $J = 7$ Hz), 1.15–2.90 (11 H, m), 3.80 (4 H, m), 5.00 (1 H, s), 5.65 (1 H, br s). Anal. ($C_{14}H_{20}O_3$) C, H. **2**: IR (KBr) 2950, 1740, 1680, 1620 cm^{-1}; IR ($CHCl_3$) 3100, 1735, 1680, 1630 cm^{-1}; NMR δ 0.95 (3 H, t, $J = 7$ Hz), 3.00 (1 H, m), 6.95 (1 H, br s). Anal. ($C_{12}H_{16}O_3$) C, H.

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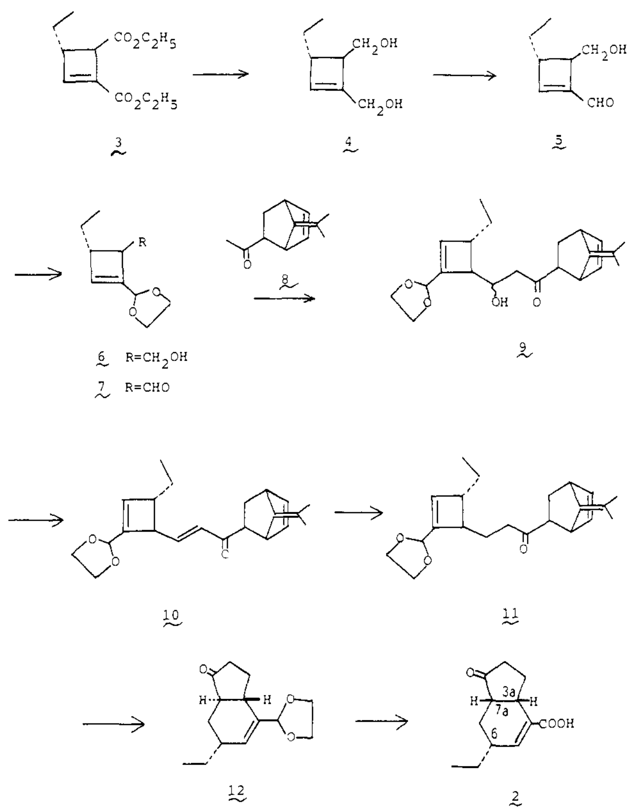
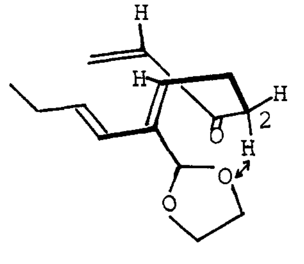
Scheme II

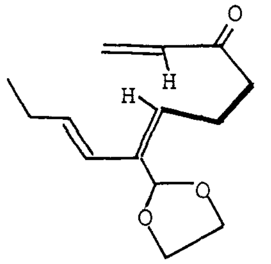


confirmed to be trans, since the coupling constant between 1-H and 4-H in the NMR spectrum is small (J = 1.5 Hz) and not suitable for cis disposition.[7] The trans geometry of **3** is necessary for formation of *E*,*E*-diene through conrotatory ring opening at a later stage. Reduction of diester **3** with lithium aluminum hydride in the presence of a small amount of ethanol[8] in ether afforded diol **4**[6] (oil,[8] 39.3%) after silica gel chromatography. This diol was converted to aldehyde **5**[6] (oil, 94.7%) by oxidation with manganese dioxide in petroleum ether (bp ~40–60 °C) and benzene while refluxing. Aldehyde **5** was transformed to ethylene acetal **6**[6] (oil, 55.2%) by refluxing with ethylene glycol in the presence of *p*-toluenesulfonic acid and using 4A molecular sieves in benzene.[9] Oxidation of **6** with Collins reagent in methylene chloride at room temperature gave oily aldehyde **7**[6] (89.9%). Methyl ketone **8**[6] was prepared from dimethylfulvene and methyl vinyl ketone by heating at ~50–60 °C in benzene under a nitrogen atmosphere (66.3%). Aldol condensation[10,11] of methyl ketone **8** with aldehyde **7** by means of lithium diisopropylamide in tetrahydrofuran (THF) at −45 °C afforded ketol **9**[6] (53.6%). Mesylation[12] of the ketol with MsCl in pyridine at room temperature and subsequent treatment with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) at ~0–5 °C after addition of toluene yielded α,β-unsaturated ketone **10**[6]. Selective reduction[13] of the conjugated double bond of **10** was accomplished by using sodium dihydrobis(2-methoxyethoxy)aluminate (60% benzene solution) in the presence of cuprous iodide in THF at ~−45 to −10 °C for 2 h to yield saturated ketone **11**[6] (oil, 34.0% from **9**).

As was expected, thermal reaction of **11** in toluene solution by heating for 30 min at 185 °C and an additional 2.5 h at ~170–180 °C[14] in a sealed tube involved three successive reactions: (1) conrotatory opening of the cyclobutene ring,[15] (2) retro-Diels–Alder reaction, eliminating fulvene,[16] and (3) intramolecular Diels–Alder reaction, affording a 92% yield of a single product, **12** (mp ~101.4–102.1 °C). The stereochemistry of the ring juncture protons in **12** was deduced to be trans, since no methine proton due to a 7a-H was observed in the NMR spectrum.[2a] Molecular models show that steric requirements in the transition state favor exo arrangement (**11a**) more than endo (**11b**), which has a severe nonbonded interaction between the 2-H and the acetal oxygens. Isomerization of product **12** with sodium methoxide afforded the cis isomer, whose NMR spectrum exhibited a signal at δ 2.80 (1 H) ascribable to the 7a-H. Jones oxidation[17] of **12** in acetone at ~0–5 °C for 5 h, accompanied by deacetalization, isomerization, and oxidation, produced (±)-coronafacic acid **2** (mp ~115–127 °C, 22.0%), whose spectral data are identical with those of a natural sample.[1,18] Since partial synthesis of coronatine (**1**) from coronafacic acid and coronamic acid has been completed,[2a] this communication constitutes a formal total synthesis of coronatine (**1**).[19]



11a



11b

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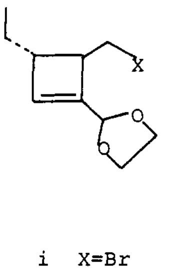
[7] Coupling constants of trans and cis vicinal protons on a cyclobutene ring normally appear in the range of ~1.7–10.7 Hz and ~4.4–11.4 Hz, respectively: Chamberlain, N. F. "The Practice of NMR Spectroscopy", Plenum Press: New York and London, 1974; pp 300.

[8] Davidson, R. S.; Grunther, W. H.; Waddington-Feather, S. M.; Lythgoe, B. *J. Chem. Soc.* **1964**, 4907.

[9] The reaction was carried out in a distilling flask, removing water as an azeotropic mixture.

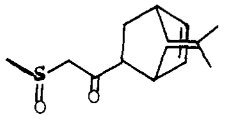
[10] Stork, G.; Kraus, G. A.; Garcia, G. A. *J. Org. Chem.* **1974**, *39*, 3459.

[11] Alkylation of keto sulfoxide iii with bromide i or mesylate ii failed because of the instability of keto sulfoxide iii during the reaction.



i X=Br

ii X=OSOCH$_3$



iii

[12] The labile mesylate of ketol **9** was not isolated and treated directly with DBU.

[13] Semmelhack, M. F.; Stanffer, R. D. *J. Org. Chem.* **1975**, *40*, 3619.

[14] The reaction temperature was settled by the fact that *trans*-3,4-dimethylcyclobutene was transformed to (*E*),(*E*)-2,4-hexadiene by heating at 175 °C: Winter, R. E. K. *Tetrahedron* **1965**, *21*, 1207. The methyl ketone **8** was decomposed to methyl vinyl ketone by heating at 170–180 °C.

[15] Extensive application of benzocyclobutene as a latent diene in the Diels–Alder reaction was reviewed in ref 4a,b.

[16] Synthetic application of the retro-Diels–Alder reaction was reviewed: Ripoll, J. L.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19. For natural product syntheses, see: Miyano, M. *Tetrahedron Lett.* **1969**, 2771. Stork, G.; Nelson, G. L.; Rouessac, F.; Gringore, O. *J. Am. Chem. Soc.* **1971**, *93*, 3901. Ho, T. L. *Synth. Commun.* **1974**, *4*, 189. Ichihara, A.; Oda, K.; Kobayashi, M.; Sakamura, S. *Tetrahedron Lett.* **1974**, 4235: *Tetrahedron* **1979**, *35*, 2861. Oda, K.; Ichihara, A.; Sakamura, S. *Tetrahedron Lett.* **1975**, 3187; *Tetrahedron* **1980**, *36*, 183. Ichihara, A.; Kimura, R.; Oda, K.; Sakamura, S. *Tetrahedron Lett.* **1976**, 4741. Ichihara, A.; Moriyasu, K.; Sakamura, S. *Agric. Biol. Chem.* **1978**, *42*, 2421. Ichihara, A.; Nio, N.; Terayama, Y.; Kimura, R.; Sakamura, S. *Tetrahedron Lett.* **19798** 3731. Ichihara, A.; Ubukata, M.; Sakamura, S. *Agric. Biol. Chem.* **1980**, *44*, 211.

[17] No attempt to oxidize the aldehyde obtained by hydrolysis of the acetal **12** was carried out since previous experiments of the Jones oxidation of an α,β-unsaturated aldehyde[3] gave coronafacic acid in low yield (13%).

[18] Coronafacic acid **2** is equilibrated in cis and trans isomers, depending on the conditions of oxidation, isolation, and recrystallization,[1] since differences in thermodynamic stabilities between *cis*- and *trans*-hydrindanones are quite small. However, treatment of the mixture of **2** with acids or sodium ethoxide affords cis isomer **2**.

The present synthesis demonstrates the utility of a latent diene–dienophile for construction of bicyclic ketones, e.g., 5,6- and 6,6-ring systems, which are useful intermediates for the synthesis of some natural products.

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(19) After our manuscript was submitted, another total synthesis of (±)-coronafacic acid by using oxy-Cope rearrangements has been reported: Jung, M. E.; Hudspeth, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2463.

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Received April 23, 1980

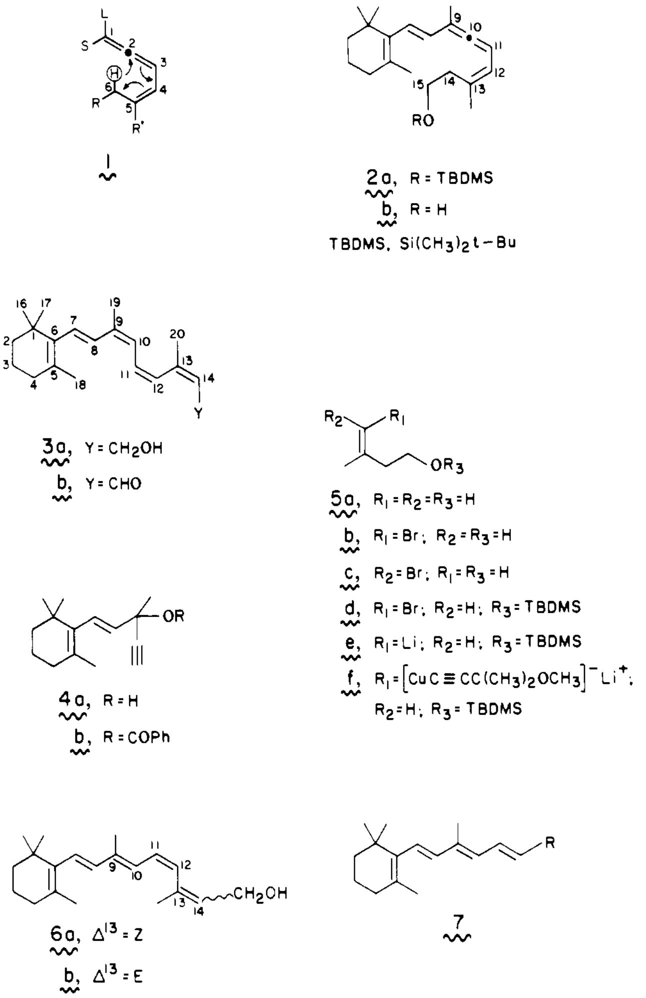
[1,5]-Sigmatropic Rearrangement of Vinylallenes: A Novel Route to Geometric Isomers of the Retinoids Possessing 11-Cis Linkages Including 9-*cis*,11-*cis*,13-*cis*-Retinal

Sir:

The thermally induced [1,5]-sigmatropic hydrogen shift of vinylallenes[1,2] of the general stereostructure **1** (Chart I) can be utilized for efficiently constructing the (3*Z*)-1,3,5-hexatriene moiety of the 1-hydroxyvitamin D system.[2] In order to examine the suitability of the vinylallene strategy for synthesizing higher order polyenes, we have directed our attention toward allenes of the vitamin A series.[3] We report the preparation and thermal studies of the 9,10-allenic retinoid **2**. The results which we wish to feature include: the first synthesis of the highly hindered 9-*cis*,11-*cis*,13-*cis*-retinol (**3a**) and -retinal (**3b**); their thermal behavior and unusual electronic spectral characteristics; the unexpected finding that the stereochemical course of the sigmatropic rearrangement of **2** is biased toward paths leading to the more hindered stereoisomeric retinols; and the gratifying observation that the 11-cis linkages of the retinols retain their stereochemical integrity under the conditions of the thermal vinylallene rearrangement.

The allene silyl ether **2a** was produced in 50% yield by the formal S_N2' coupling of propargyl benzoate **4b** with the mixed cuprate **5f**.[2,4] The sensitive propargylic benzoate **4b** was prepared by benzoylation (ether; *n*-butyllithium and then PhCOCl; 64% yield, mp 52–53 °C) of alcohol **4a**.[5] Isopentenyl alcohol (**5a**) was converted to the ~1:2 *Z*/*E* mixture **5b**–**5c**,[6] from which the pure *Z* isomer **5b** could be purified by high-pressure (Waters 500) or medium-pressure[7] liquid chromatography (LC). The bromide was subjected to protection (TBDMSCl, imidazole, DMF, 94%),[8] lithiation (2 equiv of *t*-BuLi, ether, −78 °C, 4 h),[9] and then reaction with $CuC{\equiv}C{-}C(CH_3)_2OCH_3$[9] to afford **5f**. The allene **2a** is a highly sensitive substance which was purified by rapid medium-pressure LC [silica gel, 2% pyridine/low-boiling petroleum ether (lbpe)][7] and then stored at −80 °C (N_2) in a low-temperature freezer. Deprotection of **2a** with *n*-Bu_4NF/THF (1 M, 3 h)[8] afforded the equally sensitive alcohol **2b** (37% yield; short silica column with 30% ether/2% pyridine in lbpe).

Chart I



Thermolysis of the allenic retinol **2b** (10^{-3} M in purified skellysolve B at reflux, ~69 °C, N_2, 2 h) followed by semipreparative high-pressure LC (Waters 6000A system; Whatman M9 10/50 partisil column, 9.4 mm × 50 cm; 3% isobutyl alcohol/skellysolve B) afforded in order of elution the following absolute yields of products: 9.6% 11-*cis*,13-*cis*-retinol (**6a**), 9.1% of a new isomer, 9-*cis*,11-*cis*,13-*cis*-retinol (**3a**), and 8.7% 11-*cis*-retinol (**6b**).[10] Monitoring the thermolysis under the same conditions up to 5.5 h (2537-Å UV-detection high-pressure LC) revealed that the ratio **6a**/**3a**/**6b** remained constant (1.5:1.0:1.1, uncorrected, ±5% average deviation). Each of the three retinols retained geometric integrity when subjected to the conditions of the preparative run (~69 °C, 2 h). By comparison with authentic specimens (high-pressure LC, ^1H NMR, UV),[11] 11-*cis*,13-*cis*-retinol (**6a**) and 11-*cis*-retinol (**6b**) were positively identified while the 9-*cis*-, 9-*cis*,13-*cis*-, *all-trans*-, and 13-*cis*-retinol isomers were specifically ruled out as products of the thermolysis of **2b**, **3a**, **6a**,

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(1) (a) Crowley, K. J. *Proc. Chem. Soc., London* **1964**, 17. (b) Mikolajczak, K. L.; Bagby, M. O.; Bates, R. B.; Wolff, I. A. *J. Org. Chem.* **1965**, *30*, 2983. (c) Skattebøl, L. *Tetrahedron* **1969**, *25*, 4933. (d) Bakker, S. A.; Lugtenburg, J.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 1459. (e) Minter, D. E.; Fonken, G. J.; Cook, F. T. *Tetrahedron Lett.* **1979**, 711.

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(3) (a) Nakanishi, K.; Yudd, A. P.; Crouch, R. K.; Olson, G. L.; Cheung, H.-C.; Govindjee, R.; Ebrey, T. G.; Patel, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 236. (b) Dr. G. Olson, Hoffmann-La Roche (Nutley), personal communication.

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(8) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

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(10) Thermolysis of **2a** (10^{-3} M in purified skellysolve B, ~69 °C, 2 h, under N_2; <5% starting material remained, ^1H NMR) followed by deprotection (1 M *n*-Bu_4NF/THF, 1–3 h; filtration through silica gel with 2% pyridine/30% Et_2O in low-boiling petroleum ether) and then similar preparative high-pressure LC afforded 11.5% **6a**, 14% **3a**, and 10% **6b**.

(11) Authentic specimens or precursors to authentic specimens of the *all-trans*-, 11-*cis*-, 9-*cis*-, 13-*cis*-, 11-*cis*,13-*cis*-, and 9-*cis*,13-*cis*-retinols were made available by Dr. Gary Olson and Dr. David Coffen of the Hoffmann-La Roche Co. (Nutley, NJ).

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