pounds; Dr. M. Studier for his help with mass spectra; Dr. L. Kaplan, Dr. K. Wilzback, and Dr. W. Brown for their assistance with the gas chromatography work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Supplementary Material Available. Description of a modified procedure for the preparation of XeF_2 and details for the reaction of the latter with anisole will appear following those pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-807.

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Chemistry Division **S. P. Anand**
Argonne National Laboratory **L. A. Quarterman**
H. H. Hyman[15]

Indiana University Northwest **K. G. Migliorese**
Department of Chemistry **R. Filler***
Illinois Institute of Technology
Chicago, Illinois 60616

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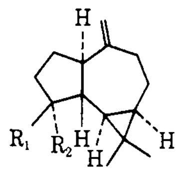
Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones. Application to the Synthesis of (−)-4-Epiglobulol and (+)-4-Epiaromadendrene[1]

Summary: Photochemical rearrangement of (−)-dehydroepimaalienone (**5**) in aqueous acetic acid produced the tricyclic hydroazulene derivative **8** which was converted into (−)-4-epiglobulol (**2b**) and (+)-4-epiaromadendrene (**1b**).

Sir: In recent years there has been considerable interest in the synthesis of tricyclic sequiterpenes having a cyclopropane ring fused to a hydroazulene ring system, and syntheses of (−)-aromadendrene (the enantiomer of **1a**),[2] (±)-globulol (**2a**),[3] and (−)-cyclocolorenone (**3**)[4] have been reported. In our synthesis of (−)-cyclocolorenone the key step involved photochemical rearrangement of the carboxy cross-conjugated dienone **4b** to establish the ring skeleton of the natural product. We now wish to report the synthesis of (−)-4-epiglobulol (**2b**) and (+)-4-epiaromadrendene (**1b**) using photochemical rearrangement of the tricyclic dienone **5** to obtain the 5/7-fused system of these compounds.



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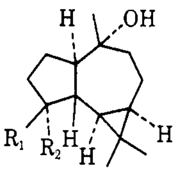

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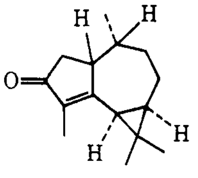

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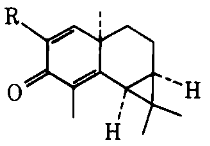
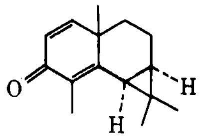
a, R_1 = H; R_2 = CH_3
b, R_1 = CH_3; R_2 = H



4a, R = H
b, R = CO_2H



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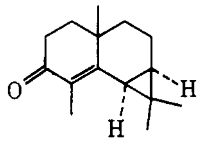

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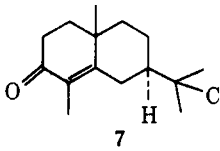

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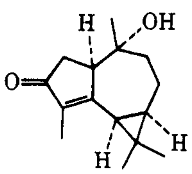
A logical precursor to **5** was (−)-epimaalienone (**6**). While this compound has been prepared in six steps from α-santonin by Ourisson and coworkers,[5] a much more convenient route involved treatment of the bicyclic chloroenone **7**, an intermediate in our recently reported synthesis of (+)-α-cyperone,[6] with sodium hydride in 1,2-dimethoxyethane. Under these conditions ring closure via the conjugate enolate of **7** occurred to give **6** in 75% yield. Oxidation of **6** with 2,3-dichloro-5,6-dicyanobenzoquinone in dioxane gave **5** (56%): bp 111–115° (0.05 mm); λ_{max} (95% EtOH) 244 nm (ϵ 10,400) and 305 (8400); ir ν_{max} (CCl_4) 1654 (conjd C=O), 1622 (conjd C=C), 1585 cm^{-1} (conjd C=C); NMR $\delta_{(CH_3)_4Si}$ (CCl_4) 1.14 (s, 6 H), 1.24 (s, 3 H), 1.84 (s, 3 H), 6.08 (d, J_{AB} = 10 Hz, 1 H), 6.78 ppm (d, J_{AB} = 10 Hz, 1 H); *m/e* (70 eV) 216.153 (calcd 216.151); $[\alpha]^{25}D$ −367° (*c* 0.132, $CHCl_3$). Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.02; H, 9.39.

In contrast to its 10 epimer, **4a**, which has been shown to be stable to direct irradiation under a variety of conditions,[4,7] **5** was found to be photochemically labile.[8] Thus, on irradiation of a solution this dienone in 45% aqueous acetic acid at room temperature for 30 min using a 450-W Hanovia high-pressure mercury lamp housed in a Pyrex probe and chromatography of the photolysis mixture on silica gel, the tricyclic hydroxy ketone **8** was isolated in 50% yield. Compound **8** showed mp 93–95°; λ_{max} (95% EtOH) 251 nm (ϵ 11,300); ir ν_{max} (CCl_4) 3420 (OH), 1700 (conjd cy-



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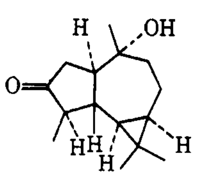

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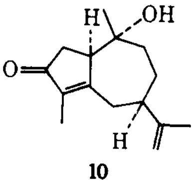

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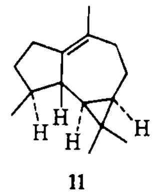

11

clopentenone), 1628 cm^{-1} (conjd C=C); NMR $\delta_{(\mathrm{CH_3})_4\mathrm{Si}}$ (CCl_4) 0.80 (s, 3 H), 0.92 (s, 3 H), 1.18 (s, 3 H), 1.68 (d of d, J = 2 Hz, 3 H), 4.90 ppm (br absorption, 1 H); m/e (70 eV) 234.162 (calcd 234.162); $[\alpha]^{25}\mathrm{D}$ −152° (c 0.111, $CHCl_3$). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.64; H, 9.48. The uv absorption maximum at 251 nm indicated that the 1 hydrogen and the cyclopropane ring had the trans relationship in the photoproduct.[9] The cis relationship of the 1 hydrogen and the 10-hydroxyl group was assigned by analogy with the stereochemical results for related cases, e.g., the α-santonin–isophotosantonic lactone type rearrangements.[7b,10] Subsequent transformations provided support for this assignment.

Our original objective was to convert **8** into (−)-globulol (**2a**) by introduction of the appropriate stereochemistry at positions 4 and 5 by reduction and conversion of the carbonyl group to a methylene group. While this objective has not been realized as yet, we have been able to prepare (−)-4-epiglobulol (**2b**) in good yield. On treatment of **8** with 2.2 equiv of lithium in liquid ammonia and addition of ammonium chloride a single dihydro ketone having the structure **9** was produced in ~97% yield. Hydroxy ketone **9** had the following spectral properties: mp 68–69°; ir $\nu_{\max}$ (CCl_4) 3600 (free OH), 3420 (hydrogen-bonded OH), 1740 cm^{-1} (cyclopentanone); NMR $\delta_{(\mathrm{CH_3})_4\mathrm{Si}}$ ($CDCl_3$) 0.99 (s, 3 H), 1.06 (d, J = 6.5 Hz, 3 H), 1.09 (s, 3 H), 1.12 (s, 3 H); m/e (70 eV) 236.175 (calcd 236.178); $[\alpha]^{25}\mathrm{D}$ −86° (c 0.072, $CHCl_3$). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.11; H, 10.27. Compound **9** was unchanged on treatment with base which indicated that the more thermodynamically stable 4 epimer had been produced. Piers and Cheng[10f] have reported that on lithium–ammonia reduction the tricyclic hydroazulene **10** related to **8** gave a dihydro product having a trans ring fusion and a 4β-methyl substituent. They pointed out that, when the ring fusion is trans, the 4α-methyl group would be a destabilized by an eclipsed interaction with C-6. While this type of interaction would also exist in the 4α epimer of **9**, examination of models suggested that the 4β-methyl substituent might be destabilized to some extent by a steric interaction with the *endo*-methyl group on the cyclopropane ring. Thus it was hoped that a mixture of 4 epimers would be present at equilibrium. However, this was not the case, and no evidence for the presence of any of the 4α epimer of **9** was obtained.

Wolff–Kishner reduction of **9** afforded a single product which after chromatography on silica gel was isolated in 55% yield. This material showed mp 49–50°; ir $\nu_{\max}$ (CCl_4) 3600 cm^{-1} (OH); NMR $\delta_{(\mathrm{CH_3})_4\mathrm{Si}}$ ($CDCl_3$) 0.94 (d, J = 5.9 Hz, 3 H), 0.96 (s, 3 H), 1.02 (s, 3 H), 1.09 ppm (s, 3 H); m/e (70 eV) 222.196 (calcd 222.198); $[\alpha]^{25}\mathrm{D}$ −16° (c 0.115, $CHCl_3$). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.04; H, 11.79. The spectral properties of this alcohol were very similar to but not identical with those of natural (−)-globulol[11] and the compounds had slightly different GLC retention times on a 6 ft × ⅛ in. 10% Carbowax K-20M on Chromosorb W column.

These results indicated that the Wolff–Kishner reduction product was 4-epiglobulol, i.e., **2b**. This was confirmed by reaction of the alcohol with thionyl chloride in pyridine at 0° followed by treatment with sodium acetate in acetic acid (to dehydrohalogenate the 10-chloro compound which was partially formed as an intermediate in the reaction). A 55% yield of a 4:1 mixture of two olefins was obtained. The major component was collected by preparative GLC using a 10 ft × ¼ in. 20% SE-30 on Chromosorb W column and exhibited identical spectral properties (ir and NMR) with those of (−)-4-epiaromadendrene.[2,12] Thus it had the structure **1b**. This olefin showed a specific rotation ($[\alpha]^{25}\mathrm{D}$ +33° (c 0.050, $CHCl_3$) of nearly the same magnitude but of opposite sign to that reported ($[\alpha]^{25}\mathrm{D}$ −31.4° (c 0.881, $CHCl_3$)) for its enantiomer.[2] The minor product obtained from dehydration of **2b** exhibited spectral properties which corresponded to the endocyclic olefin structure **11**. The formation of the exocyclic olefin as the major dehydration product of **2b** confirmed the assignment of the cis relationship between the 1-hydrogen atom and the 10-hydroxy group in the photoproduct **8**.[13]

The above results show that cyclohexadienone photolysis provides an excellent method of preparing tricyclic hydroazulenes containing a cyclopropane ring. Possible routes to allow the conversion of **8** into natural (−)-globulol (**2a**) are being explored.

Supplementary Material Available. Procedures for the preparation of new compounds reported in this paper will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W. Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-809.

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(11) We are grateful to Professors F. Šorm and P. R. Jefferies for providing us with authentic samples of (−)-globulol.

(12) We are grateful to Professor G. Büchi for providing us with copies of spectra of (−)-aromadendrene and (−)-4-epiaromadendrene.

(13) See paragraph regarding the availability of supplementary material for this paper.

School of Chemistry
Georgia Institute of Technology
Atlanta, Georgia 30332

Drury Caine*
John T. Gupton III

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Highly Fluorinated Acetylenes. Preparation and Some Cyclization Reactions

Summary: Simplified preparations of new highly fluorinated acetylenes are described and a representative model undergoes thermal cycloaddition reactions to afford a cyclohexadiene, triazole, and cyclobutene.

Sir: Highly fluorinated acetylenes have been prepared previously by multistep synthetic routes[1] that invariably in-