experiment, averages signals, and processes the data. The instrument allows the monitoring of transient phenomena in the 10-ns–100-μs time range. Further details have been given elsewhere.[35,36]

Acknowledgment. We thank the Department of Science and Technology, Government of India, Indian Institute of Technology, Kanpur, and the Office of Basic Energy Sciences of the U.S. Department of Energy for financial support of this work. We also thank Dr. N. Selvarajan for partial experimental assistance in determining the quantum yields of some of the samples.

Registry No. 9, 66933-94-6; **10**, 73367-64-3; **11**, 73395-35-4; **12**, 73367-65-4; **13**, 73464-65-0; **14**, 73367-66-5; **16**, 73367-67-6; **21**, 73367-68-7; **23**, 73395-62-7; **26**, 73367-69-8; **27**, 73367-70-1; **28**, 56585-39-8; **33**, 73367-71-2; **34**, 73367-72-3; **35**, 1096-50-0; **36**, 73367-73-4; biphenyl, 92-52-4.

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(36) L. K. Patterson and J. C. Scaiano, to be published.

Photochemical Pathways for the Interconversion of Nootkatane and Spirovetivane Sesquiterpenes[1]

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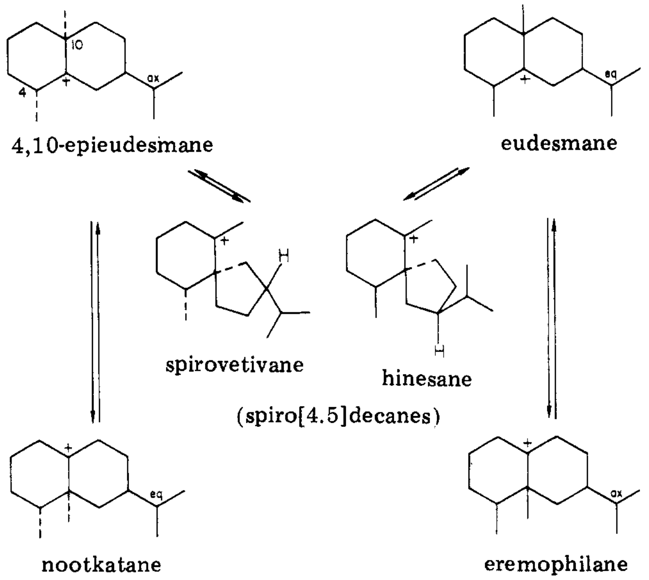
Tricyclodecenones **2a** and **2b**, prepared by irradiation of the corresponding cross-conjugated dienones in anhydrous dioxane at 254 nm, were converted into the spiro dienones **4a** and **4b**, respectively, on irradiation in aqueous acetic acid with ultraviolet light of wavelengths >300 nm. Irradiation of tricyclodecenone **11** for 30 min under similar conditions gave anhydro-β-rotunol (**12**), the bicyclic trienone **13**, and 3,4-dehydronootkatone (**10b**) in 46, 37, and 12% yields, respectively. However, monitoring of the course of the reaction by GLC indicated that **12** and **13** were formed in an initial ratio of 7:3 and that **13** and also **10b** were produced by further rearrangement of **12**. This was shown to proceed via the intermediate bicyclohexenone derivatives **16**. An independent stereospecific synthesis of the bicyclic trienone **13** from (−)-2-carone was developed. Tricyclodecenone **17**, derived from **13**, gave a mixture of **10b**, **12**, and **13**, in 20, 40, and 15% yields, respectively, when irradiated under the same conditions described for **13**. The tricyclodecenone derivative **19**, which was prepared by irradiation of 3,4-dehydro-α-vetivone (**18**) in dioxane at 254 nm, was converted exclusively into (±)-dehydro-β-vetivone (**20**) on irradiation in aqueous acetic acid with >300-nm light. Likewise, **20** was photochemically convertible into **18** via bicyclohexenones **21**. Catalytic reduction of **20** gave a 3:1 mixture of (±)-β-vetivone (**22a**) and (±)-10-epi-β-vetivone (**22b**) in low yield. Lithium–ammonia reduction of **20** gave a 3:7 mixture of **22a** and **22b** in good yield. The mechanisms of the various photochemical transformations are discussed.

Introduction

The generally accepted biogenetic pathways for interconversions of eudesmane, eremophilane (nootkatane), and spiro[4.5]decane sesquiterpenes involve Wagner–Meerwein rearrangements of appropriate carbonium ion intermediates.[2] As shown in Scheme I, methyl or methylene migrations in a eudesmane cation can yield the eremophilane or hinesane skeletons, and the corresponding rearrangements in a 4,10-epieudesmane cation can lead to the nootkatane or spirovetivane ring systems. Several examples of thermal in vitro 1,2-methyl migrations are known,[3-5] and one report of a biogenetic-like 1,2-methylene migration has appeared in the literature.[8]

Scheme I



It is well-known that cross-conjugated cyclohexadienones having a eudesmane skeleton are converted into guaiane derivatives on irradiation in protic solvents.[9,10] Consid-

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(1) This investigation was supported by Public Health Service Research Grant No. GM 15044 from the National Institute of General Medicine and No. CA 12193 from the National Cancer Institute.

(2) For a recent review, see: Marshall, J. A.; Brady, S. F.; Andersen, N. H. *Fortschr. Chem. Org. Naturst.* **1974**, *31*, 283.

(3) (a) For a recent review, see: Coates, R. M. *Fortschr. Chem. Org. Naturst.* **1976**, *33*, 73. (b) Huffman, J. W. *J. Org. Chem.* **1972**, *37*, 2736. (c) Hochstetler, A. R. *Ibid.* **1974**, *39*, 1400.

(4) (a) Kitagawa, I.; Yamazoe, Y.; Shibuya, H.; Takeda, R.; Takeno, H.; Yosioka, I. *Chem. Pharm. Bull.* **1974**, *22*, 2662. (b) Kitagawa, I., Shibuya, H.; Takeno, H.; Nishino, T.; Yosioka, T. *Ibid.* **1976**, *24*, 56.

(5) Miller, C. A.; Pinder, A. R. *J. Chem. Soc., Chem. Commun.* **1977**, 230.

(6) (a) Caine, D.; Graham, S. L. *Tetrahedron Lett.* **1976**, 2521. (b) Caine, D.; Graham, S. L.; Vora, T. T. *J. Org. Chem.*, following paper in this issue.

(7) (a) Buchi, G.; Greuter, F.; Tokoroyama, T. *J. Org. Chem.* **1962**, *27*, 827. (b) Streith, J.; Pasnelle, P.; Ourisson, G. *Bull. Soc. Chim. Fr.* **1963**, 518. (c) Ourisson, G., *Proc. Chem. Soc., London* **1964**, 274.

(8) Hikino, H.; Aota, K.; Kuwano, D.; Takemoto, T. *Tetrahedron* **1971**, *27*, 4831. (b) We thank Professor Hikino for providing us with copies of the IR and NMR spectra of anhydro-β-rotunol.

(9) For reviews, see: (a) Kropp, P. J. *Org. Photo. Chem.* **1967**, *1*, 1. (b) Schaffner, K. *Adv. Photochem.* **1966**, *4*, 81. (c) Schaffner, K. "Organic Reactions in Steroid Chemistry"; Fried, J., Edwards, J. A., Eds., Van Nostrand-Reinhold: New York, 1972; Vol. II, pp 330–338.

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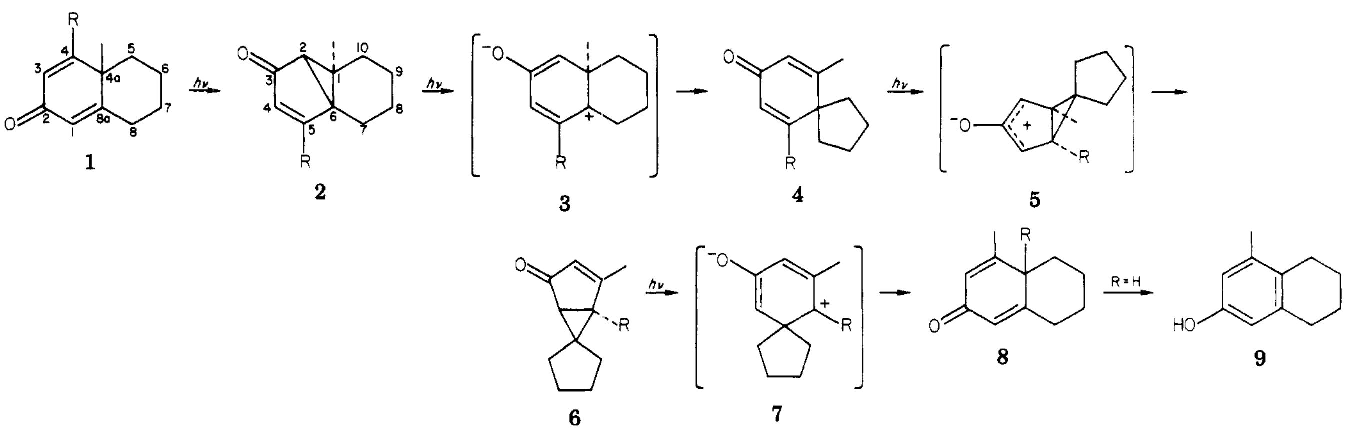
Scheme II



a, R = CH_3; b, R = H

eration of the multiple photochemical rearrangements exhibited by cross-conjugated dienones in aprotic solvents[9] suggested that interconversions of various sesquiterpene skeletons of the type shown in Scheme I might also be accomplished photochemically.[11]

As illustrated in Scheme II, tricyclodecenones (2) are the primary photoproducts obtained upon irradiation of model bicyclic dienones such as 1. These photoproducts are themselves photolabile and undergo further rearrangements, presumably via dipolar intermediates such as 3 which are considered to arise by electron excitation, cleavage of the internal bond of the cyclopropane ring, and electron demotion. The dipolar species can undergo 1,2-methylene migration to yield a spiro dienone 4 or 1,2-methyl migration which in the model case would produce the starting bicyclic dienone 1. The former pathway is normally strongly preferred except in complex systems having structural features which disfavor the production of spirocyclic systems.[9a]

Spiro dienones derived from 1,2-methinyl migrations in dipolar species analogous to 3 have been obtained by irradiation of various steriodal bicyclohexanones in dioxane with >280-nm ultraviolet light.[12] However, it has been generally observed that irradiations of simple tricyclodecenones with broad-spectrum ultraviolet light lead to bicyclohexanones related to 6 and/or further rearrangement products such as cross-conjugated dienones (8), phenols (9), and/or linearly conjugated dienones, depending upon the location of substituents and the exact photolysis conditions.[9,13]

Results

Initially, we set out to determine if photolysis conditions could be found which would allow conversion of model tricyclodecenones such as 2 into the corresponding dienones (4). Dienone **1a**, which is related to the nootkatane system since it contains a methyl substituent at C-4, was prepared by DDQ oxidation[14] of the corresponding *cis*-dimethyloctalone[15] and irradiated in anhydrous dioxane at 254 nm to produce the tricyclodecenone **2a** in 62% yield. Irradiation of **2a** in 45% aqueous acetic acid using a 450-W high-pressure mercury lamp housed in a Pyrex probe gave spiro dienone **4a** in 52% after chromatography on alumina. In this run and in subsequently described runs involving other tricyclodecenones, optimum irradiation periods were determined by monitoring the course of the reaction by GLC. Irradiations of dienone **1a** or of tricyclodecenone **2a** in anhydrous dioxane using Pyrex-filtered light gave some of the desired spiro product **4a**. However, GLC analysis indicated that complex mixtures containing several other products were produced in addition to **4a**.

It was felt that steric hindrance to the formation of **5a**, which would have the two methyl groups on the cyclopropane ring cis to each other, might be an important factor which accounted for the photostability of **4a** compared with systems that have been previously investigated.[13] Therefore, the photochemical behavior of the known ring A unsubstituted tricyclodecenone **2b**[16] was investigated. Irradiation of **2b** under the conditions used for the **2a** → **4a** conversion, followed by chromatography of the photolysis mixture, gave spiro dienone **4b** in 62% yield. Irradiation of **2b** was also carried out in 45% aqueous acetic acid, using a quartz probe to house the lamp, providing the phenol **9**[17] as the only photoproduct. Since tricyclodecenones **2a** and **2b** both gave essentially the same results, it appears that the use of long wavelength ultraviolet light transmitted via a Pyrex filter for the irradiations was the principal factor which allowed the isolation of the spiro dienones.

Next, the photochemical behavior of various bicyclic dienones with sesquiterpene carbon skeletons was examined. 3,4-Dehydronootkatone (**10b**)[18] was prepared by oxidation of nootkatone (**10a**)[19] with DDQ and converted into the corresponding tricyclodecenone **11** as described above (see Chart I for structures). After irradiation of a solution of **11** in 45% aqueous acetic acid for 30 min using Pyrex-filtered ultraviolet light, the starting material had completely disappeared and the spiro trienone **12**, the bicyclic trienone **13**, and 3,4-dehydronootkatone (**10b**) were isolated in 46, 37, and 12% yields, respectively, after chromatography on silica gel. The spiro dienone **12** proved to be identical with anhydro-β-rotunol which has been obtained from β-rotunol by reaction with phosphorus oxychloride in pyridine.[8] Anhydro-β-rotunol was later shown to be produced as a stress metabolite of blight-infected potatoes.[20]

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[10] Piers, E.; Cheng, K. F. *Can. J. Chem.* **1967**, *45*, 1591; *Ibid.* **1970**, *48*, 2234.

[11] For a preliminary publication of some of this work, see: Caine, D.; Chu, C.-Y. *Tetrahedron Lett.* **1974**, 703.

[12] Frei, J.; Ganter, J.; Kagi, D.; Kocsis, K.; Miljkovic, M.; Siewinski, A.; Wenger, R.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1966**, *49*, 1049.

[13] (a) Kropp, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 4053. (b) Kropp, P. J. *Tetrahedron* **1965**, *21*, 2183.

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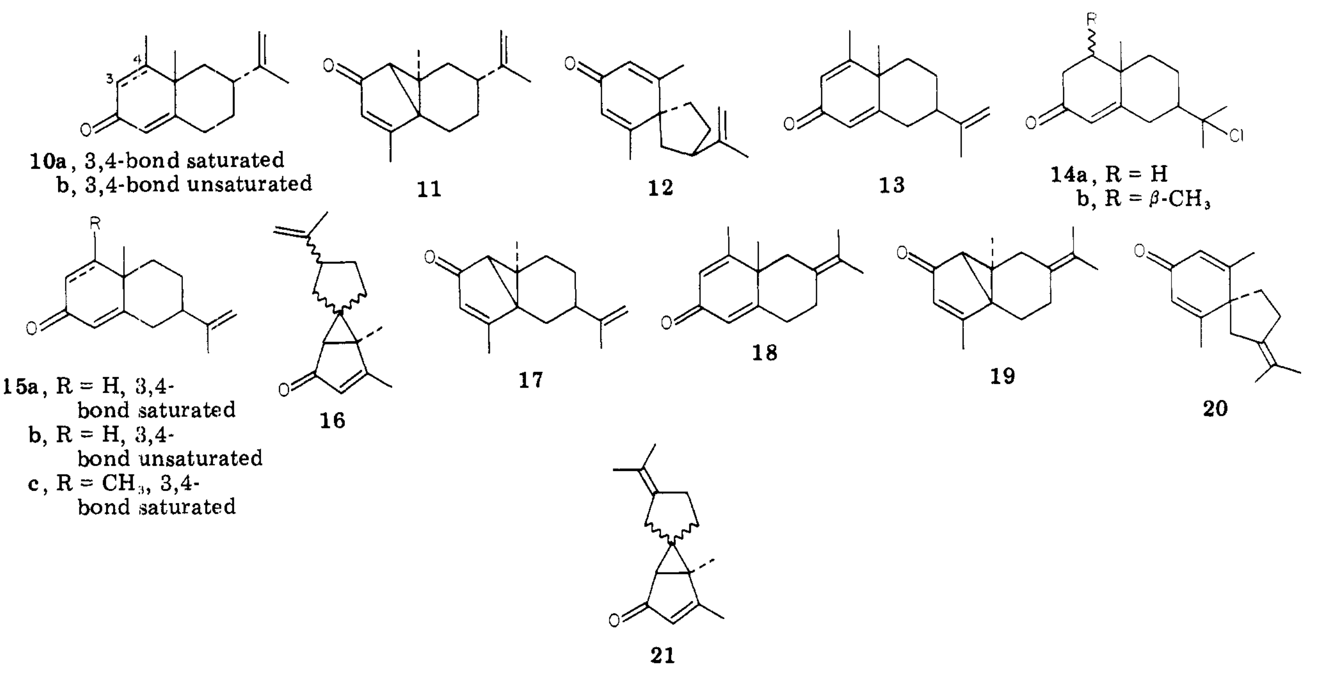
[17] Woodward, R. B.; Singh, T. *J. Am. Chem. Soc.* **1950**, *72*, 494.

[18] Pesaro, M.; Bozzato, G.; Schudel, P. *Chem. Commun.* **1968**, 1152.

[19] We are grateful to Dr. Charles Varsel of the Coca-Cola Company for providing us with a generous gift of partially purified nootkatone.

Chart I



10a, 3,4-bond saturated
b, 3,4-bond unsaturated

11

12

13

14a, R = H
b, R = β-CH$_3$

15a, R = H, 3,4-bond saturated
b, R = H, 3,4-bond unsaturated
c, R = CH$_3$, 3,4-bond saturated

16

17

18

19

20

21

The structure of bicyclic trienone **13** was established by two independent syntheses. The mixture of octalone derivatives prepared by annelation of (+)-dihydrocarvone with *trans*-3-penten-2-one[21] was oxidized with DDQ to give a 3:7 mixture of the cis trienone **13** and the corresponding trans isomer. A sample of **13** which was >85% pure was collected from this mixture by preparative GLC. A significant quantity of **13** was needed for other work.[6] Therefore, a stereospecific synthesis was developed. Dehydrohalogenation of the chloro enone **14a**, prepared as described previously,[22a] with sodium acetate in acetic acid and oxidation of the dienone product (**15a**) with DDQ in dioxane gave the trienone **15b** in 45% overall yield. Selective conjugate addition of lithium dimethylcuprate to the disubstituted, conjugated double bond in **15b**[23] gave a dienone (presumably having trans methyl groups[23]) which was directly oxidized with DDQ to give the trienone **13** in 60% overall yield.

Michael addition of (–)-2-carone to *trans*-3-penten-2-one was carried out under the conditions previously described with methyl vinyl ketone[22] in order to avoid having to introduce the 4-methyl group in a separate step. A 1,5-diketone which was converted into chloro enone **14b** upon treatment with hydrogen chloride in ethanol was obtained. However, the yield in the Michael addition step was <20% and we were unable to improve this by using a variety of different conditions, including aprotic conditions, for the reaction. The cis relationship of the methyl groups in **14b** was established by converting it to the dienone **15c** and comparing the spin–spin splitting pattern of the 3-methylene group in the presence of an NMR shift reagent with that of **10a** and a related octalone[21] which also has cis 4,4a-methyl groups.

It was shown that trienones **12** and **13** were produced directly from irradiation of tricyclodecenone **11**, while **10b** and also **13** were formed by subsequent photochemical rearrangement of spiro dienone **12**. When the course of the photolysis of **11** was monitored by GLC, **12** and **13** were formed in an initial ratio of 7:3, but this ratio began to approach unity and dienone **10b** began to appear as the irradiation was continued. When the three trienone photoproducts were irradiated separately under the conditions described for complete disappearance of tricyclodecenone **11**, the bicyclic trienones **10b** and **13** were only about 25% rearranged while over 50% of the spiro trienone **12** was converted into a ca. 1:1 mixture of **10b** and **13**. Irradiation of spiro trienone **12** in dioxane at 254 nm gave a mixture of four new photoproducts. This mixture was not separated nor were the structures of the photoproducts conclusively established; however, its GLC behavior and spectral properties indicated that it was composed of about equal amounts of four diastereomeric bicyclohexenone derivatives of the general structure **16**. On irradiation of this mixture in aqueous acetic acid using Pyrex-filtered light, dienones **10b** and **13** were produced in an initial ratio of 1:1; on irradiation for 30 min the starting materials had disappeared and **10b**, **13**, and **12** were present in a 2:3:2 ratio. A priori, the mixture of bicyclohexanones of the type **16** could have also produced the C-4a epimers of **10b** and **13**, but no evidence for such products was obtained. A possible explanation for this will be presented later.

Bicyclic trienone **13** was converted into the corresponding tricyclodecenone **17** by irradiation in dioxane at 254 nm.[6] Upon irradiation of **17** for 30 min in aqueous acetic acid using Pyrex-filtered light, a mixture of **10b**, **12**, and **13** was produced in 20, 40, and 15% yields, respectively. By monitoring the course of the rearrangement by GLC, it was found that the bicyclic trienone **10b** and the spiro trienone **12** were produced initially in a 1:5.7 ratio. As in the case of **11**, subsequent rearrangement of compound **12** accounted for the formation of the bicyclic trienone **13**.

The next compound to be investigated was 3,4-dehydro-β-vetivone (**18**). This compound has been prepared along with the corresponding fully conjugated system by oxidation of α-vetivone with DDQ.[24] However, we found that it could be obtained in ca. 85% yield by ad-

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[20] Coxon, D. T.; Price, K. R.; Howard, B.; Osman, S. F.; Kalan, E. B.; Zacharius, R. M. *Tetrahedron Lett.* **1974**, 2921.

[21] Leitereg, T. J. *Tetrahedron Lett.* **1972**, 2617.

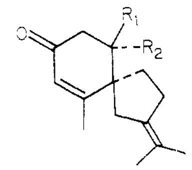
[22] (a) Caine, D.; Deutsch, H.; Gupton, J. T., III. *J. Org. Chem.* **1978**, *43*, 343. (b) Caine, D.; Gupton, J. T., III. *Ibid.* **1975**, *40*, 2654.

[23] (a) Marshall, J. A.; Brady, S. F. *J. Org. Chem.* **1970**, *35*, 4068. (b) Marshall, J. A.; Warne, T. M., Jr. *Ibid.* **1971**, *36*, 178.

[24] Marshall, J. A.; Andersen, N. H. *Tetrahedron Lett.* **1967**, 1611.

dition of hydrogen bromide to the double bond of the isopropenyl group of 3,4-dehydronootketone (**10b**) followed by dehydrohalogenation of the bromide product with tetra-*n*-butylammonium bromide and 2,6-lutidine in acetone,[25] followed by chromatography on silver nitrate impregnated silica gel. Trienone **18** was converted into the corresponding tricyclodecenone **19** in 65% yield by irradiation in anhydrous dioxane as described above. Irradiation of **19** in aqueous acid as described for **11** and **17** gave dehydro-β-vetivone (**20**)[8] as the exclusive product in 60% yield. Irradiation of **20** in dioxane at 254 nm gave a mixture of two products whose GLC behavior and spectral properties indicated that it was probably composed of a mixture of about equal quantities of bicyclohexenones of the type **21**. Irradiation of this mixture in aqueous acetic acid using Pyrex-filtered light gave racemic dehydro-α-vetivone (**18**) in 50% overall yield from **20**.

In order to carry out a complete conversion of a bicyclic sesquiterpene to its spirocyclic counterpart, methods of selective reduction of dehydro-β-vetivone **20** were investigated. When this trienone was allowed to absorb 1 mol of hydrogen, in ethanol using 5% palladium on carbon as a catalyst, GLC and spectral analysis of the hydrogenation mixture indicated that dihydro derivatives, tetrahydro derivatives, and the starting material were present in a ca. 3:2:2 ratio. It was shown by GLC analysis that the dihydro derivatives which were produced were (±)-β-vetivone (**22a**) and (±)-10-epi-β-vetivone (**22b**)[26] in a 7:3 ratio. Lithium–ammonia reduction of **20** allowed selective reduction of one of the conjugated double bonds in good yield. However, in this case racemic **22b** rather than the natural product was the major compound obtained. In a related reduction, Gunn and co-workers[27] have found that lithium–ammonia reduction of anhydro-β-rotunol (**12**) gave a mixture of four diastereoisomers in a 3:3:1:1 ratio.



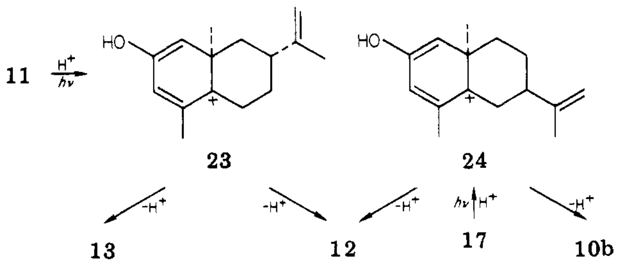
22a, $R_1 = CH_3$; $R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$

Discussion

As noted above, the spiro dienones **4a** and **4b** were isolated in good yields by irradiation of the corresponding tricyclodecenones (**2**) in aqueous acetic acid using Pyrex-filtered ultraviolet light. These compounds presumably arise via methylene migrations in intermediates analogous to **3** (Scheme II), but having the oxygen atom protonated. As is consistent with previous studies,[9,12] bicyclic dienones (**1**) which could result from 1,2-methyl migrations in similar intermediates were not observed.

The photoconversion of spiro dienones such as **4** into secondary products is probably initiated by an n → π* excitation when long wavelength ultraviolet light is employed. In aqueous acetic acid this transition would be expected to occur at a shorter wavelength than in aprotic media.[29] This may account for the relatively slow rate of rearrangement of the spiro dienones under the conditions of their formation from the corresponding tricyclodecenones.

Scheme III



The conversion of tricyclodecenone **2b** into phenol **9** with broad-spectrum ultraviolet light presumably involved the spiro dienone **4b** and the bicyclohexenone **6b** as intermediates.[9] In the O-protonated form of intermediates **7**, 1,2-methylene migration to the position para to the oxygen function is apparently the only rearrangement pathway involved. These results are consistent with those obtained for related compounds.[9]

The rearrangement of lumi-3,4-dehydronootkatone (**11**) apparently occurs via the bicyclic carbonium ion intermediate **23** (Scheme III). In this case there is competition between a 1,2-methylene migration pathway leading to anhydro-β-rotunol (**12**) and a 1,2-methyl migration pathway which gives the bicyclic trienone **13**; the initial ratio of **12** to **13** was 7:3. Although still the minor pathway, methyl migration occurred to a much greater extent than has been observed in simple B-ring unsubstituted systems. If the carbonium ion **23** adopts a conformation with the A ring planar to permit maximum overlap of the π system and if the B ring is in a normal chain form, a 1,3-diaxial methyl–isopropenyl interaction would exist. This interaction can be relieved by a 1,2-methyl migration which has the net effect of converting an axial isopropenyl group to an equatorial one. This or some other factor attributable to the cis relationships of the substituents in **23** presumably accounts for the fact that a significant amount of **13** was produced from **11**.

Irradiation of tricyclodecenone **17**, which may be regarded as a 10-epieudesmane derivative, should occur via carbonium ion intermediate **24**. The initial ratio of the methylene migration product **12** to the methyl migration product **10b** was 5.7:1. Methyl migration in **24** would also have the net effect of converting an axial isopropenyl group to an equatorial one, but this pathway, while still significant compared with ring B unsubstituted systems, was less important than that in carbonium ion intermediate **23**.

By carefully controlling the time of irradiation of **17** it is possible to build up a significant level of the major primary rearrangement product, anhydro-β-rotunol (**12**). Since **12** is separable from both **13** and **10b** by chromatography, this photochemical approach provides a relatively good synthetic route to the natural product.

Photoisomerization of the spiro dienone **12** can yield four diastereomeric bicyclohexenones (**16**). Photoinduced cleavage of the internal bond of the cyclopropane ring of these isomers can yield two possible carbonium ion intermediates, **25** and **26** (Scheme IV). Migration of either the methylene group (a) or the ethylene group (b) would be possible in these intermediates. In **25** migration of group a would give **10b**, which was observed, while migration of group b would yield the 4a-epimer of **13** (cf. **27**), which was not observed. In **26** migration of group a would yield the 4a-epimer of **10b** (cf. **28**), which was not observed,

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[25] Biale, G.; Cook, D.; Lloyd, D. J.; Parker, A. J.; Stevens, I. O. R.; Takakashi, J.; Weinstein, S. *J. Am. Chem. Soc.* **1971**, *93*, 4735.

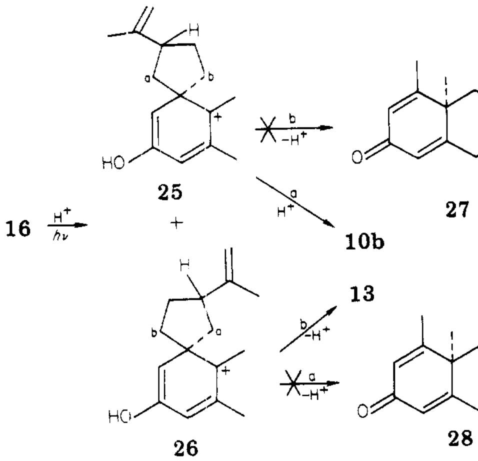
[26] McCurry, P. M.; Singh, R. K. *Tetrahedron Lett.* **1973**, 1155.

[27] Anderson, P. C.; Gunn, D. M.; Murray-Rust, J.; Murray-Rust, P.; Roberts, J. S. *J. Chem. Soc., Chem. Commun.* **1977**, 27.

[28] Caine, D.; Alejandre, A. M.; Ming, K.; Powers, W. J.; III. *J. Org. Chem.* **1972**, *37*, 706.

[29] Dyer, J. R. "Applications of Absorption Spectroscopy of Organic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1965; p 8.

Scheme IV



while migration of group b would yield **13** which was observed. Epimers **27** and **28** should be thermodynamically unstable with respect to **13** and **10b**, respectively, since in the former cases the isopropenyl groups are axial to chair conformations of the B rings while in the latter they are equatorial. Apparently, this causes the transition states leading to **27** and also **28** to be of sufficiently high energy to preclude formation of these compounds.

Irradiations of lumiproducts **19** and **20** appear to yield carbonium ion intermediates which undergo exclusive migration of the allylic methylene groups. Allylic stabilization of positive charge in the transition state would be expected to favor this process.

In summary, it has been shown that it is possible to photochemically interconvert the ring skeletons of bicyclic and spirocyclic sesquiterpenes via bicyclohexenone intermediates. It is interesting to speculate that such pathways may be involved in influencing the levels of these types of sesquiterpenes in plants. Possibly enzymatic oxidation to a ring-A dienone, photochemical rearrangement to a new ring-A dienone, and enzymatic reduction could provide an in vivo means of interconverting bicyclic and spiro systems of the nootkatane and spirovetivane type.

Experimental Section[30]

5,6,7,8-Tetrahydro-4,4a-dimethyl-2(4a*H*)-naphthalenone (1a). A solution of 20.0 g (0.11 mol) of 3,4,5,6,7,8-hexahydro-4β,4aβ-dimethyl-2(4a*H*)-naphthalenone[15] and 28.0 g (0.12 mol) of DDQ in 50 mL of anhydrous benzene containing 3.0 mL of glacial acetic was heated at reflux with stirring for 48 h. The mixture was cooled to room temperature and filtered to remove 2,3-dichloro-5,6-dicyano-*p*-hydroquinone (DDHQ). The solvent was then removed in vacuo and the residue was placed on a column of 50 g of neutral alumina and eluted with 500 mL of anhydrous ether. The ether was removed in vacuo and the residue was chromatographed on 350 g of basic alumina. Elution of the column with 5% ether–hexane afforded 4.1 g of the starting enone and continued elution with 20% ether–hexane gave 7.8 g (39%) of dienone **1a**: bp 114–119 °C (0.2 mm); UV (CH_3OH) 245 nm (ε 18400); IR (CCl_4) 1667 (α,β-unsaturated C═O), 1628 cm^{-1} (conjugated C═C); NMR (CCl_4) δ 1.28 (s, 3 H, 4a-CH_3), 1.94 (d, J = 0.5 Hz, 3 H, 4-CH_3), 5.94 (s, 2 H, 1- and 3-vinyl H's).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.76; H, 9.16. Found: C, 81.57; H, 9.16.

Irradiation of Dienone 1a. A. In Dioxane at 254 nm. A solution of 1.0 g (0.0060 mol) of dienone **1a** in 150 mL of anhydrous dioxane was irradiated with a low-pressure mercury lamp for 2.5 h. The solvent was removed in vacuo and the residue chromatographed on 25 g of basic alumina. Elution with 5% ether–hexane gave 0.62 g (62%) of tricyclodecenone **2a** and with 15% ether–hexane gave 0.13 g of the starting dienone **1a**. **2a**: bp 100–105 °C (0.2 mm); UV (CH_3OH) 234 (ε 7800), 267 nm (4300); IR (CCl_4) 1695 (α,β-unsaturated C═O), 1671 cm^{-1} (conjugated C═C); NMR (CCl_4) δ 1.15 (s, 3 H, 1-CH_3), 1.97 (d, J = 1.5 Hz, 3 H, 5-CH_3), 5.5 (m, 1 H, 4-H).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.76; H, 9.16. Found: C, 81.58; H, 9.16.

B. In Dioxane with Pyrex-Filtered Ultraviolet Light. Dienone **1a** was irradiated under the same conditions as those described in part A, except that a high-pressure mercury lamp housed in a Pyrex probe was used as the light source. After the solvent was removed in vacuo, GLC analysis (column A)[30] indicated that the photolysis mixture contained ~20% of the spiro dienone **4a** (for the characterization of the compound, see below). However, several other products were present along with **4a** and this mixture was not investigated further.

Irradiation of Tricyclodecenone 2a. A. In 45% Aqueous Acetic Acid with Pyrex-Filtered Ultraviolet Light. A solution of 0.5 g of **2a** in 240 mL of 45% aqueous acetic acid was irradiated with a high-pressure lamp housed in a Pyrex probe. After 29 min of irradiation, **2a** had completely disappeared according to GLC analysis (column A).[30] The solution was then extracted with ether (3 × 80 mL). The combined ether extracts were washed with a saturated solution of NaCl, a saturated solution of $NaHCO_3$, and water and dried. After removal of the solvent in vacuo, the residue was chromatographed on 10 g of silica gel. Elution with 20% ether–hexane gave 0.26 g (52%) of the spiro dienone **4a**: bp 115–120 °C (0.2 mm); UV (CH_3OH) 245 nm (ε 12400); IR (CCl_4) 1668 (α,β-unsaturated C═O), 1628 cm^{-1} (conjugated C═C); NMR (CCl_4) δ 2.01 (s, 6 H, vinyl CH_3's) and 5.90 (s, 2 H, vinyl H's).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.76; H, 9.16. Found: C, 81.58; H, 9.23.

B. In Anhydrous Dioxane with Pyrex-Filtered Ultraviolet Light. A solution of 0.8 g of **2a** in 150 mL of anhydrous dioxane was irradiated until the starting material had almost completely disappeared by GLC analysis (column A).[30] The solvent was then removed in vacuo. GLC analysis of the residue indicated that some of the spiro dienone **4a** had been produced, but several other products were also present. The components of this mixture were not investigated further.

Irradiation of Tricyclodecenone 2b. A. In 45% Aqueous Acetic Acid with Pyrex-Filtered Ultraviolet Light. A solution of 100 mg of tricyclodecenone **2b**[17] in 2.5 mL of 45% aqueous acetic acid was irradiated in the usual way for 40 min with a high-pressure mercury lamp in a Pyrex probe. The mixture was extracted with ether (3 × 10 mL) and the combined ether extracts were washed with a saturated solution of NaCl and a saturated solution of $NaHCO_3$ and dried. After removal of the solvent in vacuo, the residue was distilled to afford 62 mg (62%) of the spiro dienone **4b** as a colorless oil: bp 80–85 °C (0.2 mm); UV (MeOH) 238 (ε 16300), 243 nm (15700); IR (CCl_4) 1667 (α,β-unsaturated C═O), 1629 cm^{-1} (conjugated C═C); NMR (CCl_4) δ 1.93 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 5.98 (d, J = 10 Hz, 1 H), 5.99 (s, 1 H), 6.91 (d, J = 10 Hz, 1 H).

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(30) Melting and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 457 infrared spectrophotometer. Ultraviolet spectra were measured on a Beckman Model 25 spectrophotometer, using 1-cm matched cells. The ^1H NMR spectra at 60 MHz were obtained with a Varian T-60 spectrometer and at 100 MHz with JEOL fourier transform Model PFT-100 spectrometer. Chemical shifts are expressed in δ values (parts per million) relative to Me_4Si as an internal standard. Abbreviations s, d, t, and q refer to singlets, doublets, triplets, and quartets, respectively. Mass spectra were obtained with a Hitachi Perkin-Elmer Model RMU-7 or a Varian Model M-66 spectrometer. Gas–liquid chromatography was carried out with a Perkin-Elmer 881 or an Aerograph A-90-P3 gas chromatograph. The following columns were used: A, a 10 ft × 0.125 in. aluminum column packed with 20% Carbowax 20M on acid-washed Chromosorb W; B, a 6 ft × 0.25 in. stainless-steel column containing 20% Carbowax 20M on acid-washed Chromosorb W; C, 10 ft × 0.25 in. stainless-steel column packed with 20% Craig polyester on 60/80 Chromosorb W. Microanalyses were performed by Atlantic Microlabs, Inc., Atlanta, GA. A Hanovia 45-W high-pressure lamp was used as the source of broad-spectrum ultraviolet light. A 7-W Hanau NK-20 low-pressure mercury lamp was used as the source of 254-nm ultraviolet light. All irradiations were conducted by agitation of the solution with a stream of dry nitrogen for 10 min prior to and during the entire irradiation period. Solvents were removed in vacuo, using a Buchi Rotavapor rotatary evaporator. Column chromatography was carried out on grade 923 100–200 mesh silica gel or Brockman activity I 80–200 mesh acidic, basic, or neutral alumina. Anhydrous $MgSO_4$ was used as the drying agent for organic solutions.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.43; H, 8.70. Found: C, 81.22; H, 8.80.

B. In 45% Aqueous Acetic Acid Using Broad-Spectrum Ultraviolet Light. A solution of 50 mg of **2b** in 2.5 mL of 45% aqueous acetic acid was irradiated for 30 min with a high-pressure mercury lamp housed in a quartz probe. Isolation of the product as described in part A gave 31 mg (62%) of the known phenol **9**: mp 102–103 °C (lit.[16] mp 105 °C); IR (CCl_4) 3610 and 3608 (OH stretching), 2935 and 2860 (C–H stretching), 1614, 1599, 1480 and 1462 cm^{-1} (aromatic ring); NMR (CCl_4) δ 2.09 (s, 3 H, CH_3), 4.30 (br s, 1 H, OH), 6.30 and 6.35 (2 br s, 1 H each, aromatic H's).

3,4-Dehydronootkatone (10b). A solution of 15.0 g (0.069 mol) of nootkatone (**10a**), 17.0 g (0.075 mol) of DDQ, and 5 mL of glacial acetic acid in 400 mL of dry benzene was stirred and heated at reflux under nitrogen for 48 h. The mixture was cooled to room temperature and filtered to remove DDHQ. The solvent was removed in vacuo and the residue was placed on a column of 50 g of neutral alumina and eluted with 500 mL of anhydrous ether. The ether was removed in vacuo and the residue chromatographed on 300 g of basic alumina. Elution with 5% ether–hexane afforded 2.4 g of starting material **10a** and with 10, 15, and 20% ether–hexane mixtures gave 5.5 g (37%) of 3,4-dehydronootkatone (**10b**), bp 145–150 °C (0.2 mm) [lit.[18] bp 100–105 °C (0.001 mm)]. The spectral properties of **10b** were essentially identical with those reported previously.[18]

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.17; H, 9.42.

Irradiation of 3,4-Dehydronootkatone (10b). A. In Dioxane at 254 nm. A solution of 4.2 g of trienone **10b** in 150 mL of anhydrous dioxane was irradiated with a low-pressure mercury lamp for 6 h. GLC analysis (column A)[30] of the mixture indicated that the starting trienone and another product were present in a 15:85 ratio. The solvent was removed in vacuo and the residue was chromatographed on 100 g of basic alumina. Elution with 5% ether–hexane gave 2.9 g (69%) of the tricyclodecenone **11**. Further elution with mixtures of 15 and 20% ether–hexane led to the recovery of 0.47 g of **10b**. Distillation of **11** gave a yellow oil, bp 129–134 °C (0.2 mm), which was further purified by preparative GLC (column B)[30] to obtain an analytical sample: UV (CH_3OH) 234 (ϵ 3117), 268 nm (1763); IR (CCl_4) 1682 (α,β-unsaturated C=O), 1610 (conjugated C=C), 890 cm^{-1} (=CH_2); NMR (CCl_4) δ 1.15 (s, 3 H, 1-CH_3), 1.70 (s, 3 H, vinyl CH_3) 2.00 (d, J = 1 Hz, 3 H, vinyl CH_3), 4.70 (s, 2 H, =CH_2), 5.52 (br s, 1 H, 4-vinyl H).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.22; H, 9.43.

B. In 45% Aqueous Acetic Acid with Pyrex-Filtered Ultraviolet Light. A solution of 0.10 g of 3,4-dehydronootkatone (**10b**) was irradiated for 30 min with a high-pressure mercury lamp housed in a Pyrex probe. GLC analysis of the reaction mixture indicated that 75% of the starting trienone remained and that the bicyclic trienone **13** and anhydro-β-rotunol had been formed in a ca. 1:1 ratio.

Irradiation of Tricyclodecenone 11 in 45% Aqueous Acetic Acid. A solution of 2.1 g of **11** in 250 mL of 45% aqueous acetic acid was irradiated for 30 min with a high-pressure mercury lamp housed in a Pyrex probe. GLC analysis (column A)[30] of the solution revealed that no starting material was present. The mixture was extracted with five 50-mL portions of ether. The combined ether extracts were washed with a saturated solution of NaCl followed by a saturated solution of $NaHCO_3$ and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo yielded 2.06 g of a brown oil. This material was chromatographed on 50 g of silica gel. Elution with 5% ether–hexane gave 0.142 g of 3,4-dehydronootkatone (**10b**), identical in all respects with the material prepared above by oxidation of nootkatone with DDQ. Further elution with 10% ether–hexane gave 0.705 g of a 1:6 mixture of **10b** and the bicyclic trienone **13**, with 15% ether–hexane gave 0.634 g of a 1:3 mixture of **13** and the spiro trienone **12**, and with mixtures of 20 and 30% ether–hexane gave 0.472 g of spiro dienone **12**: bp 145–150 °C (bath temperature, 0.2 mm); UV (CH_3OH) 246 nm (ϵ 12 900); IR (CCl_4) 1667 (α,β-unsaturated C=O), 1629 (conjugated C=C), 892 cm^{-1} (=CH_2); NMR (CCl_4) δ 1.79 (s, 3 H, vinyl CH_3), 2.06 (s, 6 H, vinyl CH_3's), 4.76 (d, J = 1.0 Hz, 2 H, =CH_2), 5.87 (s, 2 H, vinyl H's); mass spectrum, m/e (70 eV) 216.1524 (calcd 216.514). The IR and NMR spectra of **12** were identical with those of an authentic sample.[8b]

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.02; H, 9.40.

Repeated chromatography of the mixtures afforded in total 0.252 g (12%) of **10b**, 0.943 g (46%) of spiro trienone **12**, and 0.768 g (37%) of the bicyclic trienone **13**, bp 143–150 °C (bath temperature, 0.2 mm). An analytical sample of **13** was prepared by preparative GLC (column B)[30] and showed the following spectral properties: UV (CH_3OH) 245 nm (ϵ 19 100); IR (CCl_4) 1668 (α,β-unsaturated C=O), 1631 (conjugated C=C), 890 cm^{-1} (=CH_2); NMR (CCl_4) δ 1.32 (s, 3 H, angular CH_3), 1.78 (s, 3 H, vinyl CH_3), 1.99 (s, 3 H, vinyl CH_3), 4.78 (s, 2 H, =CH_2), 5.97 (s, 2 H, 1- and 3-vinyl H's); mass spectrum, m/e (70 eV) 216.1524 (calcd 216.1514).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.20; H, 9.40.

In a similar run the course of the photolysis of **11** was monitored at 5-min intervals by GLC analysis (column A).[30] This experiment showed that anhydro-β-rotunol (**12**) and the bicyclic trienone **13** were produced in an initial ratio of 7:3. As the irradiation was continued, the ratio of **12** to **13** began to approach unity and dehydronootkatone (**10b**) began to be produced.

Synthesis of Bicyclic Trienone 13. A. Via Annelation of Dihydrocarvone with 3-Penten-2-one and Oxidation of the Products with DDQ. The procedure of Leitereg[21] was employed. A solution of 24.0 g (0.16 mol) of (+)-dihydrocarvone and 7.2 g (0.16 mol) of 52% sodium hydride in mineral oil in 250 mL of dry dioxane was heated at reflux with stirring under nitrogen for 1.5 h. The mixture was cooled to room temperature and a solution of 13.2 g (0.16 mol) of 3-penten-2-one in 50 mL of dioxane was added dropwise with stirring over 1.5 h. The mixture was stirred for 24 h at 25 °C and neutralized by addition of 5% hydrochloric acid. The mixture was extracted with three 200-mL portions of ether, and the combined ether extracts were dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the mixture was distilled to give 13.0 g (38%) of a mixture of bicyclic dienones [bp 60–117 °C (0.2mm)].

A solution of 5.0 g of the above mixture and 6.1 g (0.027 mol) of DDQ in 100 mL of anhydrous benzene containing 1 mL of glacial acetic acid was refluxed with stirring under nitrogen for 48 h. The mixture was cooled to room temperature and filtered to remove DDHQ. The solvent was removed in vacuo and the residue was placed on a column of 35 g of neutral alumina and eluted with 500 mL of ether. The solvent was removed and the residue chromatographed on 120 g of basic alumina. Elution with 5% ether–hexane gave 1.2 g of a mixture of bicyclic dienones and with 10 and 15% ether–hexane gave a mixture of the bicyclic trienone **13** and its epimer with a trans relationship of the angular methyl and isopropenyl groups in a 3:7 ratio by GLC (column A).[30] Preparative GLC (column B)[30] gave a sample containing greater than 85% of one component having the characteristic spectral properties of **13** given above.

B. From Chloro Enone 14a. A mixture of 5.0 g (0.021 mol) of the bicyclic chloro enone **14a** in 75 mL of glacial acetic acid containing 8.2 g (0.060 mol) of sodium acetate was stirred rapidly and heated at 100 °C for 1 h. The mixture was cooled to room temperature, poured into 75 mL of cold water, and extracted with two 75-mL portions of chloroform. The combined chloroform extracts were washed with two 50-mL portions of 2% aqueous KOH, one 50-mL portion of 2 N hydrochloric acid, one 50-mL portion of saturated $NaHCO_3$, and two 50-mL portions of saturated NaCl and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue distilled to give 3.95 g of a yellow oil, bp 130–140 °C (0.02 mm), which was greater than 90% one component by GLC (column A).[30] An analytical sample of dienone **15a** collected by preparative GLC (column B)[30] showed the following: UV (95% C_2H_5OH) 238 nm (ϵ 15 000); IR (CCl_4) 1668 (α,β-unsaturated C=O), 1618 (conjugated C=C), 890 cm^{-1} (=CH_2); NMR (CCl_4) δ 1.30 (s, 3 H, 4a-CH_3), 1.70 (br s, 3 H, vinyl CH_3), 4.78 (br s, 2 H, =CH_2), 5.65 (s, 1 H, vinyl H); mass spectrum, m/e (70 eV) 204.1524 (calcd 204.1515).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.19; H, 9.88.

A solution of 11.0 g of dienone **15a** and 13.5 g (0.0593 mol) of DDQ in 1350 mL of anhydrous dioxane was heated at reflux under nitrogen for 18 h. The solution was cooled to room temperature and the precipitate of DDHQ which formed was removed by filtration. The solvent was removed in vacuo and the residue was dissolved in 500 mL of ether. The ether solution was washed with five 100-mL portions of 2% aqueous KOH and two 100-mL portions of saturated NaCl and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue distilled to yield (46%) of trienone **15b**: bp 140–148 °C (0.2 mm); UV (95% C_2H_5OH) 241 nm (ϵ 18 000); IR (CCl_4) 1668 (α,β-unsaturated C=O), 1630 and 1605 (conjugated C=C), 888 cm^{-1} (=CH_2); NMR (CCl_4) δ 1.25 (s, 3 H, 4a-CH_3), 1.80 (br s, 3 H, vinyl CH_3), 4.78 (br s, 2 H, exomethylene), 5.96 (s, 1 H, 1-H), 6.02 (d, J = 10 Hz, 1 H, 3-H), 6.78 (d, J = 10 Hz, 4-H); mass spectrum, *m/e* (70 eV) 202.1371 (calcd 202.1357).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.91; H, 9.04.

Conjugate addition of lithium dimethylcuprate to trienone **15b** was carried out, using the procedure of Marshall and Brady.[23a] A solution of lithium dimethylcuprate was prepared under nitrogen by addition of 32.2 mL (0.052 mol) of 1.6 M ethereal methyllithium to a suspension of 4.88 g (0.026 mol) of CuI in 125 mL of anhydrous ether. The mixture was stirred for 10 min at 0 °C after which time the yellow precipitate of methylcopper which formed initially had completely dissolved. A solution of 2.60 g (0.0130 mol) of trienone **15b** in 100 mL of anhydrous ether was then added dropwise with stirring over 3.0 h. After the addition was complete the solution was stirred for 1 h, poured into 200 mL of a saturated aqueous solution of NH_4Cl, stirred briefly, and filtered. Dilute NH_4OH was added dropwise to the filtrate to dissolve the remaining copper salts. The phases were separated and the aqueous layer was washed with two 100-mL portions of ether. The combined ethereal extracts were washed with two 100-mL protions of saturated NaCl and dried over $MgSO_4$. The solvent was removed in vacuo to give 3.29 g (91%) of a crude dienone which presumably had a trans relationship of the 4- and 4a-methyl groups.[23]

This dienone was not purified but was subjected directly to oxidation with DDQ. A solution of 2.58 g of dienone and 2.94 g of DDQ in 350 mL of anhydrous dioxane was heated at reflux under nitrogen for 18 h. The solution was cooled to room temperature and filtered to remove the DDHQ which precipitated, and the solvent was removed in vacuo. The residue was dissolved in 150 mL of ether and extracted with five 30-mL portions of cold 2% aqueous KOH and with two 30-mL portions of saturated NaCl. The ether solution was dried over $MgSO_4$ and solvent removed in vacuo to afford 2.34 g of crude material. Chromatography on 50 g of silica gel using 30% ether–hexane as the eluant gave 1.61 g (63%) of pure bicyclic trienone **13**, identical in all respects with the product of photolysis of **11**.

3,4,5,6,7,8-Hexahydro-4β,4aβ-dimethyl-7β-isopropenyl-2-(4a*H*)-naphthalenone (15c). (−)-2-Carone (25.6 g, 0.168 mol) was reacted with 13.5 g of *trans*-3-penten-2-one according to the procedure reported previously using MVK.[22a] The crude diketone [5.2 g; bp 104–128 °C (0.5 mm); IR (CCl_4) 1710 (methyl ketone), 1685 cm^{-1} (cyclopropyl ketone)] in 25 mL of absolute ethanol was added dropwise with stirring under nitrogen to 55 mL of a saturated solution of anhydrous HCl in ethanol at 2 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. It was then poured into 50 mL of ice water and extracted with four 25-mL portions of chloroform. The combined chloroform extracts were washed with two 25-mL portions of saturated $NaHCO_3$ and one 25-mL portion of saturated NaCl and dried over $MgSO_4$. The solvent was removed in vacuo to give 7.6 g of a thick yellow oil. The product was recrystallized from pentane to give 6.0 g (14%) of 3,4,5,6,7,8-decahydro-4β,4aβ-dimethyl-7β-(1-chloro-1-methylethyl)-2(4a*H*)-naphthalenone (**14b**): mp 126–127 °C; IR (CCl_4) 1669 (α,β-unsaturated ketone), 1616 cm^{-1} (conjugated C=C); NMR (CCl_4) δ 1.00 (d, J = 6 Hz, 3 H, 4β-CH_3), 1.10 (s, 3 H, 4aβ-CH_3), 1.62 (s, 6 H, $C(CH_3)_2Cl$), 5.83 (br s, 1 H, 1-vinyl H).

Anal. Calcd for $C_{15}H_{23}OCl$: C, 70.71; H, 9.10. Found: C, 70.59; H, 9.15.

Chloro enone **14b** was dehydrohalogenated under the same conditions as those described for the corresponding compound **14a** to give bicyclic trienone **15c** in 65% yield. **15c**: bp 127–137 °C (0.25 mm); IR (CCl_4) 1670 (α,β-unsaturated C=O), 1620 (conjugated C=C), 895 cm^{-1} (=CH_2); NMR δ 0.95 (d, J = 6 Hz, 3 H, 4β-CH_3), 1.07 (s, 3 H, 4aβ-CH_3), 1.73 (t, J = 1 Hz, vinyl CH_3), 4.75 (br s, 2 H, exomethylene), 5.65 (br s, 1 H, vinyl H); mass spectrum, *m/e* (70 eV) 218.1640 (calcd 218.1665). The cis relationship of the methyl groups in **14b** and **15c** was established by examining the 100-MHz NMR spectrum of **15c** in CCl_4 in the presence of Resolve-Al $EuFOD_3$ (Aldrich Chemical Co.).

At a 3:1 ratio of substrate to the shift reagent the 3-methylene group was shifted to ca. δ 7 and well-separated from other absorptions in the spectrum. Its splitting pattern was identical with the corresponding splitting patterns observed for nootkatone and an isomeric octalone derivative also having a cis relationship of the 4- and 4a-methyl groups in the presence of tris(dipivalomethanato)europium.[21]

Irradiation of Anhydro-β-rotunol (12). A. In Dioxane at 254 nm Followed by Irradiation in 45% Aqueous Acetic Acid with Pyrex-Filtered Light. A solution of 0.10 g of anhydro-β-rotunol (**12**) in 100 mL of anhydrous dioxane was irradiated with a low-pressure mercury lamp for 6 h. GLC analysis (column A)[30] of the mixture indicated that ca. 80% of **12** had been converted to approximately equal amounts of a mixture of four new products having retention times comparable to those of tricyclodecenones such as **11**. The spectral properties (UV (CH_3OH) 227 and 266 nm) of the mixture indicated that it contained bicyclohexenones of the type **16**. Without purification this mixture was dissolved in 1.0 mL of 45% aqueous acetic acid and irradiated with a high-pressure mercury lamp in a Pyrex probe. After an irradiation period of 5 min, the mixture was analyzed by GLC (column A). This indicated that bicyclic trienones **10b** and **13** had begun to be formed in a ca. 1:1 ratio. After an irradiation period of 30 min, the short retention time peaks were no longer present and **10b**, **13**, and **12** were present in a 2:3:2 ratio.

B. In 45% Aqueous Acetic Acid with Pyrex-Filtered Light. A solution of 0.15 g of spiro trienone **12** in 2.5 mL of 45% aqueous acetic acid was irradiated for 30 min with a high-pressure mercury lamp housed in a Pyrex probe. GLC analysis (column A)[30] of the photolysis mixture indicated that the starting material was 50% converted into a ca. 2:3 mixture of 3,4-dehydronootkatone (**10b**) and bicyclic trienone **13**.

Irradiation of Bicyclic Trienone 13. A. In Anhydrous Dioxane at 254 nm. A solution of 0.90 g of **13** in 250 mL of anhydrous dioxane was irradiated for 3.5 h with a low-pressure mercury lamp. GLC analysis (column A)[30] of the photolysis mixture indicated that the starting material **13** and a new product were present in a ~1:9 ratio. The solvent was removed in vacuo and the residue was chromatographed on 25 g of silica gel. Elution with 10% ether–hexane afforded 0.60 g (65%) of the tricyclodecenone derivative **17**: bp 120–130 °C (0.5 mm); IR (CCl_4) 1689 (conjugated C=O), 1607 (conjugated C=C), 890 cm^{-1} (exo methylene); NMR (CCl_4) δ 1.15 (s, 3 H, 1-CH_3), 1.70 (s, 3 H, $C(CH_3)$=CH_2), 2.02 (d, J = 1.5 Hz, 3 H, 5-CH_3), 4.70 (br s, 2 H, =CH_2), 5.55 (br s, 1 H, =CH_2).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.14; H, 9.34.

B. In 45% Aqueous Acetic Acid with Pyrex-Filtered Ultraviolet Light. A solution of 0.15 g of trienone **13** in 2.5 mL of 45% aqueous acetic acid was irradiated for 30 min with a high-pressure mercury lamp housed in a Pyrex probe. GLC analysis (column A)[30] of the photolysis mixture indicated that ~80% of the starting trienone **13** remained and that 3,4-dehydronootkatone (**10b**) and anhydro-β-rotunol (**12**) had been formed in a 1:2 ratio.

Irradiation of Tricyclodecenone 17 in 45% Aqueous Acetic Acid with Pyrex-Filtered Light. A solution of 0.15 g of **17** in 2.5 mL of 45% aqueous acetic acid was irradiated for 30 min with a high-pressure mercury lamp housed in a Pyrex probe. Workup of the mixture in the usual way and chromatography of the mixture on silica gel led to the isolation of anhydro-β-rotunol (**12**), 2,3-dehydronootkatone (**10b**), and the bicyclic trienone **13** in 40, 20, and 15% yields, respectively.

In a similar run the course of the irradiation was monitored at 5-min intervals by GLC analysis (column A).[30] This revealed that **12** and **10b** were produced in an initial ratio of 5.7:1.

3,4-Dehydro-α-vetivone (18). A solution of 4.0 g of 3,4-dehydronootkatone (**10b**) in 50 mL of glacial acetic acid was cooled to 17 °C and stirred while 10 mL of 32% HBr in acetic acid was added slowly under nitrogen. The mixture was allowed to stir for 1.5 h at 17 °C and then for 10 min at room temperature. Ether (100 mL) was added and the mixture was neutralized with 5% aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was washed with one 100-mL portion of ether. The combined ether extracts were dried over $MgSO_4$ and the solvent was removed in vacuo to give 5.25 g of a brown oil: UV (CH_3OH) 240 nm (ε 19 000); IR (CCl_4) 1664 (α,β-unsaturated C=O), 1629 cm^{-1} (conjugated C=C); NMR (CCl_4) δ 1.32 (s, 3 H, 4a-CH_3), 1.75, 1.78 (2 s, 6 H, $C(CH_3)_2Br$), 2.01 (s, 3 H, 4-vinyl CH_3), 5.94 (s, 2 H, 1- and 3-vinyl H's).

A solution of crude bromo dienone (5.0 g, 0.017 mol) in 50 mL of acetone containing 8.1 g (0.0251 mol) of tetra-*n*-butylammonium bromide and 1.93 g (0.0181 mol) of 2,6-lutidine was stirred under nitrogen at 50 °C for 2 h. The solvent was removed in vacuo and 100 mL of ether–water (1:1) was added. The mixture was shaken, the ether layer was separated, and the aqueous layer extracted with one 50-mL portion of ether. The combined ether extracts were dried over $MgSO_4$ and the solvent was removed in vacuo to give 4.0 g of a brown oil. GLC analysis (column A)[30] indicated that this oil was an 8:1 mixture of **18** and **10b**. Chromatography of the residue on 100 g of silica gel impregnated with 10% silver nitrate gave 0.37 g of **10b** and 3.08 g (~80%) of **18** as an oil. Recrystallization from hexane afforded white prisms: mp 79–80 °C; UV (CH_3OH) 239 (ε 16 200), 263 nm (12 700); IR (CCl_4) 1663 (α,β-unsaturated C=O), 1630 cm^{-1} (conjugated C=C); NMR (CCl_4) δ 1.16 (s, 3 H, 4a-CH_3), 1.77 (br s, 6 H, =$C(CH_3)_2$), 2.01 (d, *J* = 1 Hz, 3 H, 4-CH_3), 5.93 (br s, 2 H, 1- and 3-H).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.36; H, 9.40.

Irradiation of 3,4-Dehydro-α-vetione (18) in Dioxane at 254 nm. A solution of 1.26 g (0.0058 mol) of **18** in 125 mL of anhydrous dioxane was irradiated for 5 h with a low-pressure mercury lamp. The solvent was removed in vacuo and the residue chromatographed on 40 g of basic alumina. Elution with 5% ether–hexane gave 0.75 g (61%) of tricyclodecenone **19** and elution with mixtures of 10, 15, and 20% ether–hexane gave 0.24 g of trienone **18**. Distillation of **19** gave a yellow oil: bp 133–137 °C (bath temperature, 0.2 mm); UV (CH_3OH) 232 (ε 6110), 267 nm (3300); IR (CCl_4) 1665 (α,β-unsaturated C=O), 1609 cm^{-1} (conjugated C=C); NMR (CCl_4) δ 1.16 (s, 3 H, 1-CH_3), 1.65 (br s, 6 H, =$C(CH_3)_2$), 1.98 (d, *J* = 1.3 Hz, 5-CH_3), 5.47 (br s, 1 H, 4-vinyl H).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.37; H, 9.32.

Irradiation of Tricyclodecenone 19 in 45% Aqueous Acetic Acid with Pyrex-Filtered Ultraviolet Light. A solution of 0.39 g (0.0018 mol) of **19** in 300 mL of 45% aqueous acetic acid was irradiated for 15 min with a Hanovia 450-W high-pressure mercury lamp. The solution was agitated with a stream of dry nitrogen for 10 min prior to and during the irradiation period. The solution was then extracted with three 100-mL portions of ether, and the ether layer was washed with a saturated solution of $NaHCO_3$ until the acetic acid was neutralized. The ether layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was chromatographed on 10 g of neutral alumina. Elution with mixtures of 10, 15, and 20% ether–hexane gave 0.23 g (60%) of dehydro-β-vetivone (**20**)[8] as an oil. Recrystallization of this material from hexane afforded white needles: mp 76–78 °C; UV (CH_3OH) 244 nm (ε 6400); IR (CCl_4) 1666 (α,β-unsaturated C=O), 1632 (conjugated C=C); NMR (CCl_4) δ 1.68 (br s, 6 H, =$C(CH_3)$), 1.92 (s, 6 H, 2 vinyl CH_3's), 5.80 (s, 2 H, 2 vinyl H's).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.08; H, 9.36.

Irradiation of Dehydro-β-vetivone (20) in Dioxane at 254 nm Followed by Irradiation in 45% Aqueous Acetic Acid with Pyrex-Filtered Ultraviolet Light. A solution of 94 mg of **20** in 2.5 mL of anhydrous dioxane was irradiated for 110 min with a low-pressure mercury lamp. Removal of the solvent in vacuo and GLC analysis (column A)[30] of the mixture indicated that three new products in addition to starting materials were present. Two of the new products were collected together by preparative GLC (column B).[30] This mixture showed the following: UV (CH_3OH) 227, 266 nm; IR (CCl_4) 1689 (α,β-unsaturated C=O), 1662 cm^{-1} (conjugated C=C); NMR (CCl_4) δ 1.40 (s, 3 H, CCH_3), 1.60 (s, 6 H, =$C(CH_3)_2$), 1.97 (d, *J* = 1.5 Hz, 3 H, vinyl methyl), 5.40 (br s, 1 H, vinyl H).

These spectral data indicated that a mixture of bicyclohexenones of the type **21** had been produced. In another run the mixture obtained on irradiation of 100 mg of **20** in dioxane was dissolved in 2.5 mL of 45% aqueous acetic acid and irradiated for 20 min with a high-pressure mercury lamp. After the usual workup the crude product was chromatographed on 5 g of silica gel to yield 50 mg of dehydro-α-vetivone (**18**) on elution with 20% ether–hexane.

Reduction of Dehydro-β-vetivone (20). A. By Hydrogenation over Palladium on Calcium Carbonate. A solution of 50 mg of **20** in 0.5 mL of anhydrous ethanol was injected into a mixture of 5 mg of 5% Pd on $CaCO_3$ in 5 mL of ethanol under a hydrogen pressure of 1 atm. The reaction was stopped after 1 equiv of hydrogen had been taken up. The catalyst was removed by filtration and the solvent was removed in vacuo. GLC analysis (column A)[30] revealed that a mixture of tetrahydro derivatives, a mixture of dihydro derivatives, and unreacted **20** were present in a 2:3:2. The mixture of dihydro derivatives was present in a 7:3 ratio. These materials were collected by preparative GLC (column B).[30] The major product had identical GLC behavior (columns A and C)[30] and spectral properties with an authentic sample of β-vetivone (**22a**) isolated from oil of vetiver. The minor product had essentially identical UV, IR, and 60-MHz NMR spectral properties with those of **22a**. It showed the same GLC retention time (column C)[30] relative to **22a** as that reported for 10-epi-β-vetivone (**22b**).[26]

B. With Lithium in Liquid Ammonia. A solution of 123 mg (0.570 mmol) of **20** and 42 mg (0.570 mmol) of dry *tert*-butyl alcohol in 5 mL of anhydrous ether was added dropwise with stirring to a solution of 8 mg (1.2 mmol) of lithium in anhydrous liquid ammonia at −33 °C under nitrogen. The mixture was stirred for 35 min and 0.5 g of solid NH_4Cl was added. The ammonia was allowed to evaporate and a mixture of 20 mL of ether and 30 mL of water was added. The mixture was shaken, the ether layer was separated, and the aqueous layer was extracted with 30 mL of ether. The combined ether extracts were dried over anhydrous $MgSO_4$. Removal of the ether in vacuo and distillation of the residue gave 112 mg [bp 130–135 °C (bath temperature, 0.2 mm)] of a colorless oil which was shown by GLC analysis (columns A and C)[30] to be a 3:7 mixture of racemic β-vetivone (**22a**) and racemic 10-epi-β-vetivone (**22b**).

Registry No. 1a, 74410-98-3; **2a**, 74410-99-4; **2b**, 22789-82-8; **4a**, 74411-00-0; **4b**, 19143-98-7; **9**, 3718-79-4; **10a**, 4674-50-4; **10b**, 26609-40-5; **11**, 53768-19-7; **12**, 34206-82-1; **13**, 53768-29-9; **13** 4a-epimer, 74431-64-4; **14a**, 73890-13-8; **14b**, 74411-01-1; **15a**, 13918-47-3; **15b**, 74411-02-2; **15c**, 74431-65-5; **17**, 74431-66-6; **18**, 53797-65-2; **19**, 74431-67-7; **20**, 34126-61-9; **22a**, 22196-46-9; **22b**, 42483-52-3; 3,4,5,6,7,8-hexahydro-4β,4aβ-dimethyl-2(4a*H*)-naphthalenone, 22465-74-3; (+)-dihydrocarvone, 5948-04-9; *trans*-3-penten-2-one, 3102-33-8; (−)-2-carone, 74431-68-8.