MHz, assigned from a mixture of **36a/36b**) δ 7.64–7.79 (m, 3 H), 7.39–7.46 (m, 1 H), 7.31–7.37 (m, 1 H), 7.15–7.21 (m, 1 H), 7.05–7.07 (m, 1 H), 4.79–5.00 (m, 4 H, CH_2=C, CHOCOR*, and $CHCH_3$), 2.81 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.70 (br s, 1 H, C_1H), 2.30 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 2.10 (br s, 1 H, C_6H), 1.67 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.41–1.82 (m, 4 H), 1.00–1.41 (m, 3 H), 0.75–0.86 (m, 1 H); ^{13}C NMR (100 MHz, assigned from a mixture of **36a/36b**) δ 171.95, 155.50, 149.84, 134.22, 129.60, 129.27, 127.57, 126.70, 126.35, 123.88, 118.87, 107.65, 106.12, 78.33, 72.65, 44.84, 41.01, 37.15, 25.07, 24.97, 24.04, 21.42, 18.38.

(1*S*,6*R*,7*R*)-7-[[[(*R*)-1-(β-Naphthoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (36b): ^{1}H NMR (400 MHz, assigned from a mixture of **36a/36b**) δ 7.64–7.79 (m, 3 H), 7.39–7.46 (m, 1 H), 7.31–7.37 (m, 1 H), 7.15–7.21 (m, 1 H), 7.05–7.07 (m, 1 H), 4.79–5.00 (m, 4 H, CH_2=C, CHOCOR*, and $CHCH_3$), 2.85 (ddq, J = 18, 7 and 2 Hz, 1 H, C_8H_{endo}), 2.39 (br s, 1 H, C_1H), 2.44 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 1.91 (br s, 1 H, C_6H), 1.66 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.41–1.82 (m, 4 H), 1.00–1.41 (m, 3 H), 0.86–1.00 (m, 1 H); ^{13}C NMR (100 MHz, assigned from a mixture of **36a/36b**) δ 172.07, 155.50, 149.67, 134.19, 129.60, 129.23, 127.54, 126.76, 126.35, 123.88, 118.81, 107.50, 106.07, 78.33, 72.65, 44.73, 40.80, 37.15, 25.03, 24.97, 24.01, 21.34, 18.43; HRMS (mixture of **36a/36b**) calcd for $C_{23}H_{26}O_3$ 350.1881, found 350.1920.

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Supplementary Material Available: ^{1}H NMR for compounds **20**, **23**, **26**, **28**, **31**, and **33**, ^{13}C NMR for **28**, and spectral (^{1}H NMR) and physical data for acids **4**, **5**, **12**, **13**, and **17–19** and the methyl esters of the phenoxy acids (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis and Photochemical Rearrangement of (1*R*,7a*S*)-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-5(7a*H*)-indanone

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Reaction of (1*S*,7a*S*)-1-hydroxy-7a-methyl-7,7a-dihydro-5(6*H*)-indanone (**5a**) with benzoic acid under the usual conditions of the Mitsunobu reaction gave a low yield of a 1:1 mixture of the benzoate derivatives **6b** and **5b** resulting from inversion and retention of configuration, respectively, at C-1. Under conditions in which the benzoic acid concentration was kept low, only the inversion product **6b** was obtained but the extent of conversion of the alcohol to the ester was low. The substitution of *p*-nitrobenzoic acid for benzoic led to a significant improvement in the yield of the inversion product **6c**. Several other methods of obtaining α-oxy derivatives of the type **6b–e** were explored but with little or no success. The reaction of the tosyloxy enone **5d** with azide ion and cyanide anion gave enones of the type **12** resulting from retention of configuration at C-1 largely or exclusively. The (*p*-nitrobenzoyl)oxy derivative **6c** was converted into the corresponding cross-conjugated cyclohexadienone, (1*R*,7a*S*)-1-(*tert*-butyldiphenylsiloxy)-7a-methyl-5(7a*H*)-indanone (**4a**), which was irradiated in glacial and in aqueous acetic acid. In the former solvent, the dienone system underwent photochemical rearrangement to give the 5/6-fused acetoxyl enone **14** and a 2:1 mixture of the tricyclic cyclopropyl ketone **15** and **16** in 25% and 17% yields, respectively, but in aqueous acetic acid phenolic products **18** and **20**, obtained by thermal cleavage of the 1,7a carbon–carbon bond, were obtained almost exclusively. In contrast, under the same photolysis conditions, the dienone **1a**, the C-1β epimer of **4a**, gave a mixture of photoproducts composed of the 5/6-fused hydroxy ketone **21**, the 5/6-fused acetoxy ketone **2a**, and the tricyclic conjugated cyclopropyl ketone **22** in 47%, 5%, and 15% yields, respectively.

Recently, the 1β-oxy-substituted 6/5-fused cross-conjugated cyclohexadienone **1a** was synthesized and converted into the 5/6-fused acetoxy enone **2a**, along with other photoproducts, by irradiation in glacial acetic acid.[1] It was felt that a similar photochemical rearrangement of the 3-isopropyl derivative of **1a**, i.e., **1b**, would produce the 5/6-fused acetoxy enone **2b**, which would be a useful precursor of the highly oxygenated oplopane sesquiterpene tussilagone (**3**)[2] and related compounds. However, the conversion of **2b** into **3** would require inversion of the configuration of the secondary oxygen functionality at C-7. Thus, it appeared of interest to prepare the C-1 epimer of dienone **1a**, i.e., **4a**, and to investigate its photochemical behavior.

The plan for the synthesis of dienone **4a** involved the application of the Mitsunobu inversion procedure[3] to the known chiral 1β-hydroxy enone **5a**[4] to give the corresponding 1α-hydroxy enone **6a**[5] followed by protection of the hydroxyl group as the *tert*-butyldiphenylsilyl derivative and oxidation of the enone to the dienone by the phenylselenenylation–selenoxide elimination procedure.[6]

(1) Caine, D.; Kotian, P. L.; McGuiness, M. D. *J. Org. Chem.* **1991**, *56*, 6307.
(2) Ying, B. P.; Yang, P. M.; Zhu, R. H. *Acta. Chim. Sinica* **1987**, *45*, 450; *Chem. Abstr.* **1987**, *107*, 102504n.
(3) Mitsunobu, O. *Synthesis* **1981**, 1.
(4) Micheli, R. A.; Hajos, Z. G.; Cohen, N.; Parrish, D. R.; Portland, L. A.; Sciamanna, W.; Scott, M. A.; Wehrli, P. A. *J. Org. Chem.* **1975**, *97*, 5434.
(5) Stork, G.; Kahne, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 1072.

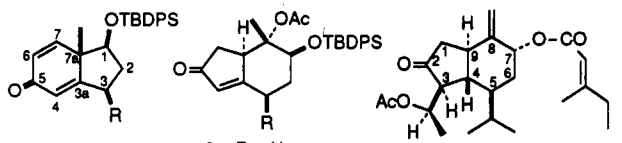
0022-3263/92/1957-6587$03.00/0

Table I. Mitsunobu Reaction of the 1β-Hydroxy Enone 5a with Aryl Acids under Various Conditions

aromatic acid	reaction condns[a]	scale (mmol)	% retention product	% inversion product	% recovered starting material
$PhCO_2H$	A	1.0	**5b** (~15)[b]	**6b** (~15)[b]	~70[b]
$PhCO_2H$	B	1.0	**5b**	**6b** (~36)[b]	~64[b]
$PhCO_2H$	B	20.0	**5b** (~11)[b]	**6b** (~21)[b]	~68[b]
p-$NO_2C_6H_4$-CO_2H	C	1.0	**5b**	**6c** (~78)[c]	
p-$NO_2C_6H_4$-CO_2H	C	20.0	**5c** (~13)[b]	**6c** (~25)[b]	~62[b]
p-$NO_2C_6H_4$-CO_2H	D	2.5	**5c**	**6c** (~82)[b]	~18[b]

[a] Key: (A) 1.2 equiv of DEAD was added over 10 min to a solution of **5a**, PPh_3, and $PhCO_2H$ in 10 mL of PhH at 25 °C; (B) a solution containing 1.2 equiv each of Ph_3P and $PhCO_2H$ in 10 mL of PhH was added dropwise over 30 min to a solution of **5a** and DEAD (1.6 equiv) in 10 mL of PhH at 70 °C; (C) 1.2 equiv of DEAD was added over 10 min to a solution of **5a**, PPh_3 (1.2 equiv), and p-$NO_2C_6H_4CO_2H$ (1.2 equiv) in 20 mL of PhH at 80 °C; and (D) 5.0 equiv of DEAD added over 10 min to a solution of **5a**, Ph_3P (5.0 equiv), and p-$NO_2C_6H_4CO_2H$ (5.0 equiv) in 55 mL of PhH at 80 °C. [b] The percentages were determined by integration of the ^1H NMR absorptions of the C-1α and C-1β protons in **5** and **6**, respectively. [c] Isolated yield after chromatography on silica gel.

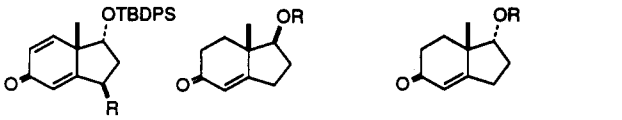
Although no experimental details were provided, Stork and Kahne[6] have reported that the enone **6a** is available from the enone **5a** by the Mitsunobu reaction. However, in our hands this reaction proved to be quite troublesome, particularly when it was run on a modest scale. Herein we wish to report the results of our studies on the conversion of **5a** into **6a** by the Mitsunobu reactions and other methods as well as the synthesis and photochemical rearrangement of dienone **4a**.



1a. R = H
b. R = i-Pr

2a. R = H
b. R = i-Pr

3



4a. R = H
b. R = i-Pr

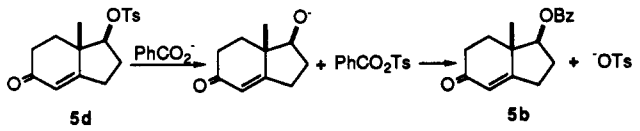
5a. R = H
b. R = Bz
c. R = p-NO_2Bz
d. R = Ts
e. R = $C_6H_{11}NHC{=}NC_6H_{11}$
f. R = -CHO
g. R = TBDPS

6a. R = H
b. R = Bz
c. R = p-NO_2Bz
d. R = -CHO
e. R = $Me_3C_6H_2CO$-
f. R = TBDPS

The results of Mitsunobu reactions of alcohol **5a** with aromatic acids to produce enone ester derivatives **5** and/or **6** resulting from retention and inversion of the configuration at C-1, respectively, are shown in Table I. In most of the reactions, the ratios of the products were obtained by integration of the ^1H NMR spectra of the crude reaction mixtures. In each case the C-1α proton in enone esters of the type **5** appeared as a doublet of doublets (J = 7.8, 11 Hz) and the C-1β proton in the isomers of the type **6** appeared as a doublet (J = 4.0 Hz) in the ^1H NMR spectrum. Also, the vinyl protons at C-4 exhibited different chemical shifts in the 1β- and 1α-isomers.

Subjection of enone **5a** to standard Mitsunobu conditions (A, Table I) on a 1.0 mmol scale gave a ca. 1:1 mixture of the benzoyl derivatives **5b** and **6b** along with the unreacted starting material in a ca. 30:70 ratio. When benzoic acid and triphenylphosphine were added to a solution of

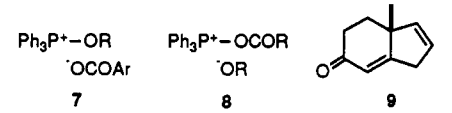
Scheme I



5d **5b**

5a and DEAD in benzene at 70 °C, the only product obtained was the inversion product **6b**, but the percentage of conversion was rather low (~35%).[7] However, when the reaction was run on a larger scale, e.g., 20 mmol, a substantial amount of the retention product **5b** was again observed and the extent of conversion to the ester products was also low. During the course of the work, Martin and Dodge[8] reported that the substitution of p-nitrobenzoic acid for benzoic acid resulted in significantly improved yields in Mitsunobu inversions of hindered secondary alcohols. Indeed, the use of this more acidic acid provided a very significant improvement in the yield of the inversion product **6c** when the reaction was conducted on a 1.0 mmol scale, but upon scale up of the reaction to 20 mmol the retention and inversion products **5c** and **6c** were produced in a 1:2 ratio and the yield of **6c** was considerably lower. However, by using a 5-fold excess of p-nitrobenzoic acid, DEAD, and triphenylphosphine and conducting the reaction on a 2.5 mmol scale, only the desired inversion product **6c** and unreacted **5a** were obtained in an 82:18 ratio.

The results of mechanistic studies by Walker and co-workers,[9a] Hughes and co-workers,[9b] and Camp and Jenkins[9c] have shown that the Mitsunobu reaction proceeds via a series of complex equilibria involving the alkoxyphosphonium ion pair **7**, which favors inversion of configuration, and the acyloxyphosphonium ion pair **8**, which favors retention of configuration. By use of ^{31}P NMR, Camp and Jenkins[9c] demonstrated that intermediate **7** is favored to a greater extent than **8** when more acidic acids than benzoic acid are employed. The present results support the findings of Martin and Dodge[8] that p-nitrobenzoic acid is the reagent of choice for effecting Mitsunobu inversion of hindered secondary alcohols.[10]



7 **8** **9**

In addition to the Mitsunobu reaction, several other possible methods of obtaining derivatives of the α-hydroxy enone **6a** were investigated. Various derivatives of enone **5a** were prepared and reacted with carboxylate salts or carboxylic acids. Treatment of the 1β-(tosyloxy) enone **5d**[11] with sodium benzoate in dimethyl sulfoxide (DMSO) under the conditions described by Cooper and Yankee[12] gave the benzoate **5b** resulting from retention of configuration at C-1 in 70% yield along with 9% of the dienone **9** resulting from β-elimination of tosic acid and 22% un-

(6) Reich, H. S.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

(7) Substitution of mesitoic acid for benzoic acid under these same conditions led to a moderate increase in the yield of the α-mesitoate ester compared with the benzoate ester **6b**. However, the mesitoate ester was found to be very difficult to hydrolyze to the corresponding hydroxy enone **6a**.

(8) Martin, S. F.; Dodge, J. A. *Tetrahedron Lett.* **1991**, *32*, 3017.

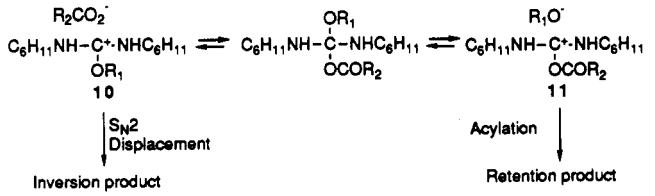
(9) (a) Varasi, M.; Walker, K. A. M.; Maddox, M. L. *J. Org. Chem.* **1987**, *52*, 4235. (b) Hughes, D. L.; Reamer, R. A.; Bergan, J. J.; Grabowski, E. J. J. *J. Am. Chem. Soc.*, **1988**, *110*, 6487. (c) Camp, D.; Jenkins, I. D. *J. Org. Chem.* **1989**, *54*, 3045, 3049.

(10) The use of aliphatic acids such as formic or crotonic acid in place of the aromatic acids in Mitsunobu reactions of **5a** gave poorer results.

(11) The enantiomer of the tosyloxy enone **5d** is a known compound, see: Inubushi, Y.; Kikuchi, T.; Ibuka, T.; Tanaka, K.; Saji, I.; Tokane, K. *Chem. Pharm. Bull.* **1974**, *22*, 349.

(12) Cooper, E. L.; Yankee, E. W. *J. Am. Chem. Soc.* **1974**, *96*, 5876.

Scheme II



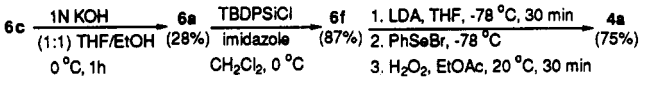
reacted starting material **5d**. It is possible that this reaction occurs by nucleophilic displacement of the tosylate group by the benzoate anion with retention of configuration (see discussion below). However, another possible mechanism for the formation of benzoate **5b**, which involves initial attack of the benzoate anion on the sulfur atom of the tosylate group, is shown in Scheme I.

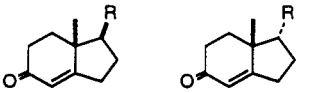
Kaulen[13] has shown that isourea derivatives of secondary alcohols undergo "inverting esterification" upon reaction with formic and other aliphatic acids. However, when the isourea derivative **5e** was reacted with formic acid in refluxing toluene, no inversion product was obtained. Instead, ^{1}H NMR analysis of the crude product indicated that the β-(formyloxy) enone **5f** and the β-hydroxy enone **5a** were present in a ca. 2:1 ratio. The latter compound probably arose from hydrolysis of the unreacted isourea derivative **5e** during aqueous workup. The substitution of benzoic acid for formic acid led to the production of a ca. 1:1:2 mixture of the inversion product **6b**, the retention product **5b**, and the β-hydroxy enone **5a**. Interestingly, when mesitoic acid was employed in a similar reaction, the only ester product was the α-(mesitoyloxy) enone **6e**; in this run enone **6e** and hydroxy enone **5a** were produced in a ca. 2:3 ratio.

Thus, the course of these reactions was very dependent upon the steric bulk of the carboxylic acid employed. A possible explanation for the observed results is that an equilibrium involving the ion pairs **10** and **11** is involved (Scheme II). Nucleophilic displacement of dicyclohexyl urea by the carboxylate anion in ion pair **10** would lead to the expected inversion product, but if this process is slow as it would be if the isourea is derived from a hindered alcohol, the alkoxide anion may undergo acylation with retention of configuration via ion pair **11**. The rate of the nucleophilic displacement reaction may not be highly dependent upon the size of R_2, i.e., the bulkiness of the carboxylate anion. However, the rate of the acylation reaction via ion pair **11** would be expected to decrease as the size of R_2 is increased. Perhaps this accounts for the fact that formic acid in which R_2 is a hydrogen atom gave exclusively the retention product and mesitoic acid in which R_2 is a bulky mesityl group gave only the inversion product, while benzoic acid in which R_2 is a phenyl group gave a mixture of the two products.

Other oxygen nucleophiles such as potassium nitrite[14] and potassium trimethylsilanoate[15] were also reacted with the tosyloxy enone **5d**, but mixtures of products containing little, if any, of the desired inversion products were obtained. Upon reaction with sodium cyanide in DMSO, the enantiomer of the tosyloxy enone **5d** has been found to give the cyano enone resulting from retention of configuration at C-1 in over 80% yield.[11] We have confirmed this result using the tosyloxy enone **5d** and obtained the 1β-cyano enone **12a** also in 80% yield. Because the C-1 proton α to the cyano group is relatively acidic, the formation of the retention product has been explained by assuming that epimerization of the initially formed inversion product, e.g., the α-cyano enone **13a**, occurred during the reaction.[16] In order to reduce the possibility of epimerization of the C-1 substituent from the α to the β configuration, sodium azide was employed as the nucleophile. In this case a ca. 1.4:1 ratio of the 1β and 1α azido enones **13b** and **12b** was obtained in 80% yield. Thus, it appears that retention of configuration is favored kinetically in substitution reactions with both the cyanide and the azide anions.

Scheme III





12a. R = CN
b. R = N_3

13a. R = CN
b. R = N_3

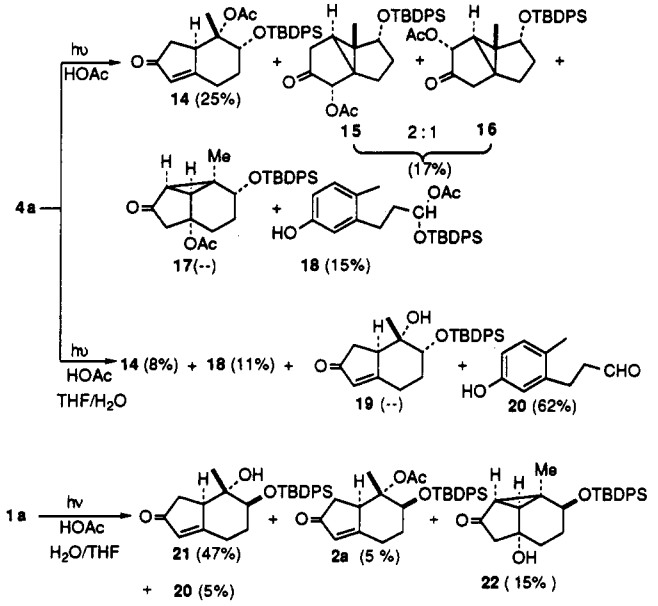
The formation of products with retention of configuration in these reactions of **5d** may result from a double inversion process with the solvent serving as the first nucleophile or possibly these displacement reactions have an S_N1 component which can provide the retention products directly. Although the 3a,4-double bond in **5d** is electron deficient because it is conjugated with the carbonyl group, it may provide some homoallylic stabilization of the carbocation which could arise via ionization of the tosyloxy group prior to attack of the nucleophile.

The protected α-oxy dienone **4a** was obtained from the (*p*-nitrobenzoyl)oxy enone **6c** by the three-stage reaction sequence shown in Scheme III. Unfortunately, the hydrolysis of the *p*-nitrobenzoate proceeded in only 28% yield.

As shown in Scheme IV solutions of dienone **4a** in glacial or aqueous acetic acid were irradiated for 1.0 h using a 450-W high-pressure mercury lamp housed in a water-cooled Pyrex probe to give mixtures of photoproducts which were separated by chromatography on silica gel. Irradiation of **4a** in glacial acetic acid yielded the 5/6-fused acetoxy ketone **14** and a 2:1 mixture of the tricyclic acetoxy ketones **15** and **16** in 25% and 17% yields, respectively. The structures of these compounds were readily established by ^{1}H NMR analysis. Compound **14** resulted from cleavage of the internal bond of the cyclopropane ring of the mesoionic Zimmerman–Schuster intermediate[17] by the solvent while compounds **15** and **16** resulted from trapping of the intermediate with the cyclopropane ring intact.[1] The photochemical behavior of dienone **4a** in acetic acid was similar to that of the epimeric dienone **1a** except that none of the expected tricyclic conjugated cyclopropyl ketone **17** was obtained. It was assumed that the epimer of **17** arose from **1a** via a 1,4-sigmatropic rearrangement of an excited state cyclopropyl intermediate followed by conjugate addition of acetic acid to a highly strained tricyclic enone intermediate.[1,18] It is not clear why **17** is not produced from **4a**. However, it may be worth pointing out that examination of a model of the putative enone precursor of **17** revealed that a strong steric interaction exists be-

(13) Kaulen, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 773.
(14) (a) Latrell, R.; Lohaus, G. *Liebigs Ann. Chem.* **1974**, 901. (b) Raduchel, B. *Synthesis* **1980**, 292.
(15) Laganis, E. D.; Chenard, B. L. *Tetrahedron Lett.* **1984**, *25*, 5831.
(16) Heathcock, C. H.; Graham, S. L.; Pirring, M. C.; Plavac, F.; White, C. T. *The Total Synthesis of Natural Products*, ApSimon, J., Ed.; John Wiley & Sons: New York, 1983; Vol. 5, p 513.
(17) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527.
(18) Caine, D.; Gupton, J. T., III; Ming, K.; Powers, W. J., III *J. Chem. Soc., Chem. Commun.* **1973**, 469.

Scheme IV



tween the α methyl group and the α-OTBDPS group which is not present when the OTBDPS group is β. This steric interaction could raise the energy of the transition state for the 1,4-sigmatropic rearrangement sufficiently to prevent its occurrence.

The phenolic hemiacetal acetate **18** was also isolated in 15% yield from the photolysis of **4a**. As was observed for the SEM-protected dienone related to **1a**,[1] this compound was produced by thermal cleavage of the 1,7a carbon–carbon bond of **4a** by acetic acid.

In an attempt to prepare a 5/6-fused hydroxy enone related to the acetoxy enone **14**, dienone **4a** was irradiated in a 1:1 water–THF solution containing 6% acetic acid. Under these conditions, photochemical rearrangement of the dienone system did not compete very effectively with thermal cleavage of the 1,7a carbon–carbon bond. Thus, the acetoxy enone **14** was the only photoproduct isolated, and it was obtained in very low yield, i.e., 8%, and none of the expected hydroxy enone **19** was isolated. The major reaction products were the phenolic aldehyde **20** and the phenolic hemiacetal acetate **18**, which were produced in 62% and 11% yields, respectively.

Interestingly, it was found that photolysis of the β-oxy dienone **1a** in aqueous acetic acid proceeded smoothly to give the 5/6-fused hydroxy enone **21** in 47% yield, the 5/6-fused acetoxy enone **2** in 5% yield, and the conjugated cyclopropyl ketone **22** in 15% yield. The phenolic aldehyde **20** resulting from thermal cleavage of the 1,7a carbon–carbon bond of the dienone was obtained in only 5% yield in this case. Thus, the configuration of the δ-oxy substituent at C-1 can profoundly affect the rates of the competing photochemical and thermal processes in these systems.

Further work on the synthesis and photochemical reactions of 3-isopropyl-substituted dienones such as **1b** and **4b** is in progress.

Experimental Section

General. Benzoic acid, *p*-nitrobenzoic acid, mesitoic acid, triphenylphosphine, DEAD, DCC, DMAP, Ts-Cl, *tert*-butyldiphenylsilyl chloride, diphenyl diselenide, Br_2, NaN_3, *n*-butyllithium (2.5 M in hexane), 30% H_2O_2, and imidazole were purchased from Aldrich Chemical Co. or Fisher Scientific Co. and used without further purification. CH_2Cl_2, diisopropylamine, DMSO, dioxane, and triethylamine were distilled over CaH_2 prior to use. THF and diethyl ether were freshly distilled from sodium/benzophenone ketyl. Toluene and benzene were distilled over sodium metal. Acetic acid, ethyl acetate, and hexane were distilled prior to use.

^1H NMR and ^{13}C NMR spectra were recorded on 200- and 360-MHz spectrometers ($CDCl_3$ solvent, TMS internal standard). IR spectra were recorded in $CHCl_3$, $CDCl_3$, or CCl_4 solution using NaCl solution cells. Mass spectra (MS) were obtained using electron-impact ionization. Reaction products were purified by flash column chromatography using silica gel (support grade catalyst 951) purchased from Aldrich Chemical Co. Analytical samples were prepared by preparative TLC performed on precoated 1-mm thickness 20-cm × 20-cm silica gel plates purchased from Merck, Inc.

All air- and moisture-sensitive reactions were conducted under a prepurified nitrogen atmosphere in flame-dried glassware. Anhydrous solvents were transferred via syringe. All solutions were dried over anhydrous $MgSO_4$, and the solvents were removed in vacuo using a rotary evaporator operated at water aspirator pressure.

(1*R*,7a*S*)-1-(Benzoyloxy)-7a-methyl-7,7a-dihydro-5-(6*H*)-indanone (6b). Method A. A solution of 0.17 g (1.0 mmol) of (+)-(1*S*,7a*S*)-1-hydroxy-5(6*H*)-7a-methyl-7,7a-dihydroindanone (**5a**), 0.3 g (1.1 mmol) of triphenylphosphine, and 0.14 g (1.1 mmol) of benzoic acid in 10 mL of benzene at rt under N_2 was added dropwise 0.19 mL (1.2 mmol) of DEAD over a period of 10 min. The mixture was stirred at rt for 36 h, and the solvent was removed in vacuo. ^1H NMR analysis of the crude product showed 15% of β-(benzoyloxy) compound **5b** resulting from retention of configuration at C-1 and 15% of α-(benzoyloxy) compound **6b** resulting from inversion of configuration at C-1 were formed and 70% of the starting alcohol **5a** was present.

Method B (1.0 mmol Scale). A solution of 0.17 g (1.0 mmol) of compound **5a** and 0.28 g (1.6 mmol) of DEAD in 10 mL of benzene was heated to about 70 °C under nitrogen, and a solution of 0.32 g (1.2 mmol) of triphenylphosphine and 0.15 g (1.2 mmol) of benzoic acid in 10 mL of benzene was added dropwise over 30 min. The mixture was heated at 70 °C for 20 h and cooled to rt, and the solvent was removed in vacuo. ^1H NMR analysis of the crude product showed that 36:64 mixture of the α-benzoyloxy derivative **6b** and the starting alcohol was present. The β-(benzoyloxy) compound **5b** resulting from retention of configuration at C-1 did not appear to be formed. Purification of the mixture by preparative TLC gave pure **6b**, which was homogeneous on TLC analysis, R_f 0.35 (30% ethyl acetate in hexane): ^1H NMR (360 MHz) δ 1.30 (s, 3 H), 1.82 (ddd, J = 2, 5.3, 13 Hz, 1 H), 2.07 (m, 1 H), 2.24 (m, 1 H), 2.42 (m, 2 H), 2.56 (m, 1 H), 2.80 (m, 2 H), 5.32 (d, J = 4.5 Hz, 1 H), 5.96 (s, 1 H), 7.45 (m, 2 H), 7.58 (m, 2 H), 7.97 (m, 1 H); IR ($CHCl_3$) 2980, 1710, 1660, 1650, 1250, cm^{-1}; HRMS m/z calcd for $C_{17}H_{18}O_3$ (M^+) 270.1256, obsd 270.1240.

Method B (20.0 mmol Scale). Reaction was carried out as described above for method B on a 20 mmol scale. ^1H NMR of the crude reaction mixture showed that 11% of β-(benzoyloxy) compound **5b** resulting from retention of configuration at C-1 and 21% of α-(benzoyloxy) compound **6b** resulting from inversion of configuration at C-1 were formed and that 68% of the starting alcohol **5a** was present.

(1*R*,7a*S*)-1-[(*p*-Nitrobenzoyl)oxy]-7a-methyl-7,7a-dihydro-5(6*H*)-indanone (6c). Method C (1.0 mmol Scale). To a refluxing solution of 0.17 g (1.0 mmol) of compound **5a**, 0.33 g (1.25 mmol) of triphenylphosphine, and 0.21 g (1.25 mmol) of *p*-nitrobenzoic acid in 20 mL of benzene under nitrogen was added 0.23 mL (1.25 mmol) of DEAD dropwise over a 10-min period. The mixture was refluxed for 1.0 h and cooled to rt, and the solvent was removed in vacuo. The residue was taken up in 20 mL of diethyl ether, and the ethereal solution was washed with two 20-mL portions of a saturated aqueous solution containing 1:1 $NaHCO_3$ and K_2CO_3 and with 20 mL of brine. The organic layer was dried and filtered, and the solvent was removed in vacuo to give 1.4 g of a crude residue. This material was purified by flash column chromatography (10% ethyl acetate in hexane) to give 0.37 g (78%) of the α-[(*p*-nitrobenzoyl)oxy] compound **6c**. A small portion of this material was crystallized from an ether hexane mixture to give white crystals: mp 112–116 °C: ^1H NMR

(360 MHz) δ 1.33 (s, 3 H), 1.84 (m, 1 H), 2.13 (m, 2 H), 2.52 (m, 3 H), 2.82 (m, 2 H), 5.36 (d, J = 4.5 Hz, 1 H), 5.97 (s, 1 H), 8.14 (d, J = 8.8 Hz, 2 H), 8.30 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (360 MHz) δ 21.72, 28.27, 28.74, 28.89, 32.92, 47.06, 83.06, 123.23, 123.68, 130.68, 135.22, 150.70, 163.85, 174.07, 198.45; IR ($CDCl_3$) 3030, 1735, 1670, 1615, 1535, 1485, 1355, 1230, 1220, 750, 730, 660 cm^{-1}; HRMS m/z calcd for $C_{17}H_{17}O_5N$ (M^+) 315.1107, obsd 315.1074.

Method C (20.0 mmol Scale). To a refluxing solution of 3.32 g (20 mmol) of compound **5a**, 6.56 g (25 mmol) of triphenylphosphine, and 4.18 g (25 mmol) of *p*-nitrobenzoic acid in 20 mL of benzene under N_2 was added 4.1 mL (26 mmol) of DEAD dropwise over 10 min. The mixture was refluxed for 1.0 h and cooled to rt, and the solvent was removed in vacuo. Workup in the manner as described for method C gave an orange brown crude residue. ^{1}H NMR analysis of the crude product showed that 11% of (*p*-nitrobenzoyl)oxy compound **5c** resulting from retention of configuration at C-1 and 25% of (*p*-nitrobenzoyl)oxy compound **6c** resulting from inversion of configuration at C-1 were formed and that 64% of the starting alcohol **5a** was present.

Method D. To a refluxing solution of 0.42 g (2.5 mmol) of compound **5a**, 3.32 g (12.5 mmol) of triphenylphosphine, and 2.12 g (12.5 mmol) of *p*-nitrobenzoic acid in 55 mL of benzene under N_2 was added 2 mL (12.5 mmol) of DEAD dropwise over 10 min. The mixture was refluxed for 1.0 h and cooled to rt, and the solvent was removed in vacuo. Workup of the residue in the manner as described in method C gave 8.2 g of crude material. ^{1}H NMR analysis of the crude product showed that a mixture containing the (*p*-nitrobenzoyl)oxy derivative **6c** and the starting alcohol **5a** in a 82:18 ratio was present. None of the (*p*-nitrobenzoyl)oxy compound **5c** resulting from retention of configuration at C-1 was obtained in this run.

(1S,7aS)-1-[(*p*-Nitrobenzoyl)oxy]-7a-methyl-7,7a-dihydro-5(6H)-indanone (5c). To a solution of 0.08 g (0.5 mmol) of compound **5a** in 5 mL of CH_2Cl_2 at 0 °C were added 0.09 mL (0.63 mmol) of triethylamine, 0.11 g (0.6 mmol) of *p*-nitrobenzoyl chloride, and 0.02 g (0.13 mmol) of DMAP. The resulting solution was stirred at 0 °C for 2.0 h and then at rt for 12 h. The reaction mixture was washed with 5 mL of saturated aqueous sodium bicarbonate and 5 mL of brine. The organic layer was dried and filtered and the solvent removed in vacuo to give 0.19 g of crude residue. This crude residue was crystallized from an ethyl acetate–hexane mixture to give 0.14 g (89%) pale yellow crystals of **5c**: mp 141–143 °C: ^{1}H NMR (360 MHz) δ 1.34 (s, 3 H), 2.08 (m, 3 H), 2.46 (m, 4 H), 2.86 (m, 1 H), 5.10 (dd, J = 8, 9.5 Hz, 1 H), 5.86 (s, 1 H), 8.21 (d, J = 8.8 Hz, 2 H), 8.31 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (360 MHz) δ 16.88, 26.41, 26.63, 33.06, 34.32, 44.95, 82.43, 123.64, 123.88, 130.69, 135.24, 150.67, 164.15, 171.85, 198.23; IR ($CDCl_3$), 2995, 1735, 1670, 1615, 1540, 1475, 1385, 1355, 1280, 1210, cm^{-1}; HRMS m/z calcd for $C_{17}H_{17}O_5N$ (M^+) 315.1107, obsd 315.1119.

(1S,7aS)-1-(Tosyloxy)-7a-methyl-7,7a-dihydro-5(6H)-indanone (5d). To a solution of 0.41 g (2.5 mmol) of compound **5a** in 25 mL of CH_2Cl_2 at 0 °C was added 1.05 mL (7.5 mmol) of triethylamine, 0.57 g (3 mmol) of TsCl, and 0.08 g (0.63 mmol) of DMAP. The resulting solution was stirred at 0 °C for 2.0 h and then at rt for 12 h. The reaction mixture was washed with 20 mL of saturated aqueous $NaHCO_3$ and 20 mL of brine. The organic layer was dried and filtered and the solvent removed in vacuo to give a crude residue. Subjection of the crude to flash column chromatography (30% ethyl acetate in hexane) gave 0.55 g (70%) of pure **5d**: ^{1}H NMR (360 MHz) δ 1.19 (s, 3 H), 2.03 (m, 4 H), 2.39 (m, 3 H), 2.47 (s, 3 H), 2.74 (m, 1 H), 4.42 (dd, J = 8, 10 Hz, 1 H), 5.77 (s, 1 H), 7.36 (d, J = 8 Hz, 2 H), 7.81 (d, J = 8 Hz, 2 H).

Reaction of (1S,7aS)-1-(Tosyloxy)-7a-methyl-7,7a-dihydro-5(6H)-indanone (5d) with Sodium Benzoate. A solution of 0.18 g (0.57 mmol) of tosylate **5d** and 0.53 g (3.67 mmol) of sodium benzoate in 10 mL of anhydrous DMSO was heated at 80–90 °C for 12 h under N_2. The reaction mixture was cooled to rt and poured into 10 mL of cold water. The aqueous solution was extracted with ether (3 × 10 mL). The combined organic extracts were washed with 10 mL of brine, the organic layer was dried and filtered, and the solvent was removed in vacuo to give 0.13 g of a crude residue. ^{1}H NMR analysis of the crude product showed only the β-(benzoyloxy) compound **5b** resulting from retention of configuration at C-1 was formed. Purification of the mixture by flash column chromatography (20% ethyl acetate in hexane) gave 0.10 g (65%) pure **5b**.

(1R,7aS)-1-Cyano-7a-methyl-7,7a-dihydro-5(6H)-indanone (13a). To a solution of 0.64 g (2 mmol) of tosylate **5d** in 5 mL of DMSO was added 0.15 g (3.1 mmol) NaCN, and the mixture was stirred at rt for 2 h. The reaction mixture was then poured into 15 mL of ice–water and extracted with $CHCl_3$ (3 × 15 mL). The combined organic extracts were washed with 15 mL of water, the organic layer was dried and filtered, and the solvent was removed in vacuo to give a crude residue. ^{1}H NMR (200 MHz) analysis of the crude residue showed ^{1}H NMR absorptions at δ 1.19 (s, 3 H), 5.85 (s, 1 H) as reported previously by Ibegami and co-workers.[11]

***N,N'*-Dicyclohexylisourea Derivative of (1S,7aS)-1-Hydroxy-7a-methyl-7,7a-dihydro-5(6H)-indanone (5e).** To a solution of 0.83 g (5.0 mmol) of **5a** in 3.0 mL of anhydrous dioxane was added 1.24 g (6.0 mmol) of DCC and 3 mg of CuCl. The reaction mixture was heated at 50 °C under N_2 for 48 h and cooled to rt and the solvent removed in vacuo. NMR analysis of the residue showed that the isourea derivative **5e** was produced in quantitative yield. This product was used as such without further purification. It showed the following characteristic ^{1}H NMR absorptions: ^{1}H NMR (200 MHz) δ 4.84 (t, J = 8.2 Hz, 1 H), 5.78 (s, 1 H); IR (neat) 3330, 2960, 2850, 2120, 1665, 1570, 1445, 1375, 1365, 1315 cm^{-1}.

(1R,7aS)-1-(Mesitoyloxy)-7a-methyl-7,7a-dihydro-5-(6H)-indanone (6e). To a refluxing solution of 2.0 mmol of **5e** in 5 mL of toluene under N_2 was added a solution 0.39 g (2.4 mmol) of mesitoic acid in 5 mL of toluene dropwise with stirring over 10 min. The reaction mixture was heated at reflux for 20 h and cooled to rt, the dicyclohexyl urea which precipitated was filtered off, and the precipitate was washed with 5 mL of CH_2Cl_2. The filtrate and washings were combined, and the solvents were removed in vacuo. The residue was dissolved in 10 mL of ether, and the solution was washed with saturated aqueous $NaHCO_3$ (2 × 10 mL) to remove the excess acid and 10 mL of brine. The organic layer was dried and the solvent removed in vacuo. ^{1}H NMR analysis of the crude material showed that a 43:57 mixture of the α-(mesitoyloxy) enone **6e** and the alcohol **5a** was present. A small portion of the crude material was purified by preparative TLC to give the pure α-(mesitoyloxy) compound **6e**: ^{1}H NMR (360 MHz) δ 1.28 (s, 3 H), 1.81 (m, 1 H), 2.31 (m, 1 H), 2.27 (s, 9 H), 2.3–2.83 (m, 6 H), 5.29 (d, J = 4.4 Hz, 1 H), 5.86 (s, 1 H), 6.85 (s, 2 H); ^{13}C NMR (360 MHz) δ 19.78, 20.09, 21.02, 21.70, 28.33, 28.40, 28.95, 32.83, 46.68, 82.18, 122.92, 128.51, 130.49, 134.94, 135.66, 139.52, 169.39, 173.52, 174.70, 198.65; IR ($CDCl_3$) 2980, 2920, 2880, 1730, 1660, 1610, 1250 cm^{-1}; HRMS m/z calcd for $C_{20}H_{24}O_3$ (M^+) 312.1726, obsd 312.1739.

Reaction of *N,N'*-Dicyclohexylisourea Derivative of (1S,7aS)-1-Hydroxy-7a-methyl-7,7a-dihydro-5(6H)-indanone (5e) with Formic Acid. To a solution of 5.0 mmol of **5e** in 10 mL of toluene under N_2 was added 0.70 g (5.75 mmol) of formic acid. The reaction mixture was heated at reflux for 20 h and cooled to rt. The dicyclohexyl urea which precipitated was filtered off, and the precipitate was washed with 10 mL of CH_2Cl_2. The filtrate and washings were combined, and the solvents were removed in vacuo. The residue was dissolved in 20 mL of ether, and the solution was washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and 20 mL of brine. The organic layer was dried, and the solvent was removed in vacuo. ^{1}H NMR analysis of the crude material showed that a 68:32 mixture of the β-(formyloxy) enone **5f** and the alcohol **5a** was present. The α-(formyloxy) compound **6d** resulting from inversion of configuration at C-1 did not appear to be formed. A small portion of the crude material was purified by preparative TLC to give the pure β-(formyloxy) compound **5f**: ^{1}H NMR (200 MHz) δ 1.22 (s, 3 H), 1.80–2.18 (m, 4 H), 2.40–2.60 (m, 3 H), 2.81 (m, 1 H), 4.93 (dd, J = 7.5, 10 Hz, 1 H), 5.83 (s, 1 H), 8.12 (s, 1 H).

Reaction of *N,N'*-Dicyclohexylisourea Derivative of (1S,7aS)-1-Hydroxy-7a-methyl-7,7a-dihydro-5(6H)-indanone (5e) with Benzoic Acid. To a solution of 5.0 mmol of **5e** in 10 mL of toluene was added a solution 0.23 mL (6 mmol) of formic acid in 10 mL of toluene dropwise with stirring over 10 min. The reaction mixture was heated at reflux for 20 h and cooled to rt. The dicyclohexyl urea which precipitated was filtered off, and the precipitate was washed with 10 mL of CH_2Cl_2. The filtrate

and washings were combined, and the solvent was removed in vacuo. ^{1}H NMR analysis of the crude product showed that 29% of β-(benzoyloxy) compound **5b**, resulting from retention of configuration at C-1, and 25% of α-(benzoyloxy) compound **6b**, resulting from inversion of configuration at C-1, was formed and 46% of the alcohol **5a** was present.

(1*S*,7a*S*)-1-Azido-7a-methyl-7,7a-dihydro-5(6*H*)-indanone (12b). To a solution of 0.32 g (1 mmol) of tosylate **5d** in 10 mL of DMSO was added 0.33 g (5.0 mmol) of NaN_3. The resulting solution was heated at 80–90 °C for 20 h under N_2. The reaction mixture was cooled to rt and poured into 10 mL of cold water. The aqueous solution was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with 10 mL of brine, the organic layer was dried and filtered, and the solvent was removed in vacuo to give 0.2 g of a crude residue. Subjection of the mixture to flash column chromatography (25% ethyl acetate in hexane) gave an initial fraction containing 0.043 g (23%) of the pure β-azido compound **12b** [^{1}H NMR (360 MHz) δ 1.13 (s, 3 H), 1.87 (m, 2 H), 2.16 (m, 2 H), 2.47 (m, 3 H), 2.74 (m, 1 H), 3.53 (dd, *J* = 7.8, 11 Hz, 1 H), 5.77 (s, 1 H); ^{13}C NMR (360 MHz) δ 16.30, 26.24, 26.87, 33.01, 34.48, 45.88, 70.24, 123.37, 172.93, 198.30; IR (CCl_4) 2970, 2930, 2180, 1670, 1375, 1260 cm^{-1}; HRMS *m/z* calcd for $C_{10}H_{13}N_3O$ (M^+) 191.1059, obsd 191.1045], a second fraction containing 0.095 g (50%) of a 1:1 mixture of the β-azido compound **12b** and its α epimer **13b**, and a third fraction containing 0.014 g (7%) of a 17:83 mixture of **12b** and **13b**. The **12b**/**13b** ratios for the second and third fractions were determined by integration of the H-1 absorptions in their ^{1}H NMR spectra. The spectral properties of **13b** were deduced from analysis of the third fraction as follows: ^{1}H NMR (360 MHz) δ 1.20 (s, 3 H), 1.78 (m, 1 H), 2.04 (m, 1 H), 2.36 (m, 4 H), 2.71 (m, 2 H), 3.78 (d, *J* = 4.8 Hz, 1 H), 5.86 (s, 1 H); ^{13}C NMR (360 MHz) δ 22.25, 27.84, 28.23, 29.31, 32.98, 47.43, 71.12, 123.40, 173.63, 198.41; IR (CCl_4) 2960, 2920, 2100, 1670, 1375, 1260 cm^{-1}; HRMS *m/z* calcd for $C_{10}H_{13}N_3O$ (M^+) 191.1059, obsd 191.1052. The overall yield of **12b** and **13b** was 80%, and the ratio of the two products was approximately 3:2.

(1*R*,7a*S*)-1-Hydroxy-7a-methyl-7,7a-dihydro-5(6*H*)-indanone (6a). To a solution of 0.07 g (0.22 mmol) of compound **6c** in 1 mL of 1:1 THF–ethanol was added dropwise with stirring at −10 °C 0.35 mL of 1 N KOH. The reaction mixture was stirred at −10 °C for 1 h, and solvent was removed in vacuo. The black residue was treated with 5 mL of saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined, washed with 5 mL of brine, dried, and filtered, and the solvent was removed in vacuo to give 0.17 g of a crude oil. This material was purified by preparative TLC (75% ethyl acetate in hexane) to give 0.01 g (28%) of the pure α-hydroxy enone **6a**: ^{1}H NMR (200 MHz) δ 1.12 (s, 3 H), 1.78 (m, 3 H), 2.40 (m, 4 H), 2.71 (m, 2 H), 4.01 (d, *J* = 4.5 Hz, 1 H), 5.91 (s, 1 H); ^{13}C NMR (360 MHz) δ 21.48, 27.91, 28.14, 31.26, 33.01, 47.86, 79.50, 123.35, 176.18, 199.20; IR ($CHCl_3$) 3610, 3450, 3010, 2980, 2940, 1660, 1220, 910 cm^{-1}; HRMS *m/z* calcd for $C_{10}H_{14}O_2$ (M^+) 166.0994, obsd 166.0990.

(1*R*,7a*S*)-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-7,7a-dihydro-5(6*H*)-indanone (6f). To a solution of 0.06 g (0.36 mmol) of the α-hydroxy enone **6a** in 2 mL of CH_2Cl_2 were added 0.08 g (1.1 mmol) of imidazole and 0.11 mL (0.43 mmol) of *tert*-butyldiphenylsilyl chloride. The solution was stirred at rt for 24 h, washed with 2 mL of cold 10% HCl to remove the excess imidazole, and then washed with saturated aqueous $NaHCO_3$ (2 × 2 mL) and brine (2 mL). The organic layer was dried, and the solvent was removed in vacuo to give 0.25 g of a crude pale yellow oil. This material was purified by flash column chromatography (20% ethyl acetate in hexane) to give 0.13 g (87%) of the α-(*tert*-butyldiphenylsiloxy) enone **6f**: ^{1}H NMR (360 MHz) δ 1.01 (s, 3 H), 1.05 (s, 9 H), 1.59 (m, 2 H), 1.93 (m, 1 H), 2.53 (m, 5 H), 4.09 (d, *J* = 4 Hz, 1 H), 5.92 (s, 1 H), 7.39 (m, 6 H), 7.63 (m, 4 H); ^{13}C NMR (360 MHz) δ 19.34, 21.42, 26.92, 28.30, 28.87, 31.01, 33.21, 48.47, 81.26, 122.66, 127.59, 129.67, 133.52, 134.25, 135.73, 177.18, 199.31; IR ($CHCl_3$) 3030, 2970, 2950, 1661, 1210, 910 cm^{-1}; HRMS *m/z* calcd for $C_{22}H_{23}O_2Si$ ($M - C_4H_9$ (*tert*-butyl)) 347.1467, obsd 347.1479.

(1*R*,7a*S*)-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-5-(7a*H*)-indanone (4a). To a solution of LDA (2.13 mmol) in 10 mL of THF at −78 °C was added dropwise with stirring 0.69 g (1.7 mmol) of compound **6f** in 7.5 mL of THF over 10 min. The solution was stirred for an additional 30 min at −78 °C. A freshly prepared solution of 2.21 mmol of phenylselenenyl bromide in 10 mL of THF was added all at once at −78 °C and the reaction mixture stirred at that temperature for 15 min. The reaction mixture was allowed to warm to rt and quenched by addition of 10 mL of cold saturated aqueous NH_4Cl. The aqueous layer was extracted with (2 × 10 mL) ether, and the combined organic layers were then washed with cold 2% HCl (10 mL), cold saturated $NaHCO_3$ solution (10 mL), and brine (10 mL), dried ($MgSO_4$), and filtered. The solvent was then removed in vacuo to give a dark brown residue containing 1.14 g of the crude 6-(phenylselenenyl) derivative of the enone **6f**. This material was dissolved in 10 mL of ethyl acetate, the solution was cooled to 20 °C, 0.58 g (5.1 mmol) of 30% H_2O_2 diluted with 1.0 mL of water was added dropwise with stirring over 10 min, and the mixture was stirred for 2 h at 20 °C (the color of the reaction mixture changed from dark brown to yellow during this time). The reaction mixture was then poured into ice-cold water (10 mL), and the organic layer was separated and washed with cold saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (10 mL). The combined aqueous layers were extracted with 10 mL of ethyl acetate, and the combined organic layers were dried ($MgSO_4$) and filtered. Removal of the solvent in vacuo gave 0.91 g of the crude dienone **4a** as pale yellow oil, which was purified by flash column chromatography (25% diethyl ether in hexane containing 5% triethylamine) to give 0.51 g (75%) of pure dienone **4a** as an oil: ^{1}H NMR (360 MHz) δ 0.91 (s, 9 H), 1.03 (s, 3 H), 1.82 (m, 1 H), 2.11 (m, 1 H), 2.68 (m, 2 H), 4.25 (d, *J* = 4.4 Hz, 1 H), 6.15 (dd, *J* = 1.5, 10 Hz, 1 H), 6.24 (d, *J* = 1.5 Hz, 1 H), 6.70 (d, *J* = 10 Hz, 1 H), 7.40 (m, 6 H), 7.59 (m, 4 H); ^{13}C NMR (360 MHz) δ 19.26, 24.24, 26.79, 27.29, 31.78, 53.43, 80.06, 123.67, 127.60, 127.69, 129.22, 129.75, 129.89, 152.07, 172.78, 187.60; IR ($CDCl_3$) 2960, 2940, 2860, 1665, 1635, 1610 cm^{-1}; HRMS *m/z* calcd for $C_{22}H_{21}O_2Si$ ($M - C_4H_9$) 345.1311, obsd 345.1297.

Irradiation of (1*R*,7a*S*)-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-5(7a*H*)-indanone (4a) in Glacial Acetic Acid. A solution of 225 mL of glacial acetic acid and 2.0 mL of acetic anhydride was placed in a 250-mL capacity cylindrical glass vessel and agitated with a stream of prepurified N_2 for 5 min while being irradiated with a 450-W high-pressure mercury lamp housed in a Pyrex probe. Then 0.51 g (1.26 mmol) of the dienone **4a**, diluted with a small volume of ether (10 mL) to permit easy transfer, was introduced via a cannula. Irradiation was continued for 1.0 h until the starting material had disappeared as evidenced by TLC analysis of an aliquot of the solution. The solvent was then removed in vacuo using a rotary evaporator and then using a vacuum pump at ~0.5 Torr. The residue was dissolved in 25 mL of ether, and the solution was washed with 2 × 25 mL of saturated $NaHCO_3$ (to remove the last traces of acetic acid) and with 25 mL of brine. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give 0.53 g of a mixture of photoproducts. Subjection of the mixture to flash column chromatography (20% ethyl acetate in hexane) gave as an initial fraction containing 0.11 g (19%) of a mixture of tricyclic acetoxy ketones **15** and **16** in a 2:1 ratio as determined by NMR spectroscopy: ^{1}H NMR (360 MHz) δ 0.77 (s, 1.3 H, CH_3 in **16**), 0.81 (s, 1.9 H, CH_3 in **15**), 1.08 (s, 9 H), 1.28 (m, 2 H), 1.54–1.78 (br abs, 2 H), 2.00 (d, *J* = 7 Hz, 0.7 H), 2.06 (s, 1.9 H, OAc in **15**), 2.14 (s, 1.3 H, OAc in **16**), 2.18 (d, *J* = 19.5 Hz, 0.92 H), 2.66 (d, *J* = 20 Hz, 0.3 H, C-4 H in **16**), 2.86 (dd, *J* = 20, 6.6 Hz, 0.7 H, C-6 H in **15**), 4.26 (m, 1 H), 4.49 (s, 0.6 H, C-1 H in **15**), 4.58 (s, 0.3 H, C-1 H in **16**), 7.37 (m, 6 H), 7.68 (m, 4 H); IR ($CHCl_3$) 3030, 2940, 2920, 2860, 1745, 1740 cm^{-1}; HRMS *m/z* calcd for $C_{24}H_{25}O_4Si$ ($M - C_4H_9$ (*tert*-butyl)) 405.1522, obsd 405.1527. Further elution of the column gave a second fraction which contained 0.09 g (15%) of the hemiacetal acetate **18**: ^{1}H NMR (360 MHz) δ 1.10 (s, 9 H), 1.73 (s, 3 H), 1.94 (m, 2 H), 2.22 (s, 3 H), 2.63 (m, 2 H), 5.3 (s, 1 H, of OH), 6.10 (t, *J* = 4.8 Hz, 1 H), 6.57 (dd, *J* = 8, 2.4 Hz, 1 H), 6.62 (d, *J* = 2.4 Hz, 1 H), 6.92 (d, *J* = 8 Hz, 1 H), 7.42 (m, 6 H), 7.69 (m, 4 H); ^{13}C NMR (360 MHz) δ 19.25, 20.85, 26.46, 26.80, 26.98, 37.33, 93.29, 112.66, 117.01, 127.69, 129.81, 131.49, 132.68, 135.75, 135.87, 137.30, 153.86, 169.68, IR ($CDCl_3$) 3600, 3400, 3070, 2960, 2930, 2860, 1735, 1670, 1610, 1590 cm^{-1}; HRMS *m/z* calcd for $C_{24}H_{25}O_4Si$ ($M - C_4H_9$ (*tert*-butyl)) 405.1522, obsd 405.1530. Further elution of the column gave a third fraction

which contained 0.17 g (29%) of the 5/6-fused acetoxy ketone **14**: ^{1}H NMR (360 MHz) δ 1.10 (s, 9 H), 1.18 (s, 3 H), 1.49 (m, 1 H), 1.73 (s, 3 H), 1.78 (m, 1 H), 2.47 (m, 3 H), 2.67 (m, 1 H), 3.78 (d, J = 6 Hz, 1 H), 4.90 (s, 1 H), 5.93 (s, 1 H), 7.42 (m, 6 H), 7.68 (m, 4 H); ^{13}C NMR (360 MHz) δ 17.23, 19.46, 22.17, 24.10, 27.02, 28.96, 36.48, 45.49, 71.44, 85.51, 127.49, 129.11, 129.71, 129.96, 133.16, 133.44, 135.97, 169.90, 180.00, 208.93; IR ($CHCl_3$) 3080, 2960, 2900, 2870, 1740, 1710, 1675, 1625, 1470, 1000 cm^{-1}; HRMS m/z calcd for $C_{24}H_{25}O_4Si$ (M – C_4H_9 (*tert*-butyl)) 405.1522, obsd 405.1512.

Irradiation of (1*R*,7a*S*)-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-5(7a*H*)-indanone (4a) in Aqueous Acetic Acid. A solution of 0.85 g (11.25 mmol) of dienone **4a** containing 9% of the unoxidized 6/5-fused enone **6f** in 120 mL of THF was placed in a 250-mL capacity cylindrical glass vessel and agitated with a stream of prepurified N_2 while 120 mL of water was added slowly. To the turbid mixture was added 15 mL of glacial acetic acid. The resulting clear solution was irradiated for 1.0 h with a 450-W high-pressure mercury lamp housed in a Pyrex probe. The reaction mixture was then poured into 50 mL of ether, the organic layer was separated, and the aqueous layer was extracted with ether (3 × 25 mL). The combined ethereal extracts were washed with saturated $NaHCO_3$ (5 × 25 mL) and 50 mL of brine. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give 5.83 g of a mixture of photoproducts. Subjection of the mixture to flash column chromatography (20–30% ethyl acetate in hexane) gave as an initial fraction 0.31 g of *tert*-butyldiphenylsilanol. Further elution of the column gave a second fraction which contained 0.09 g of unoxidized 6/5-fused enone **6f**, a third fraction which contained 0.09 g (11%, based on unrecovered starting material) of the hemiacetal acetate **18**, a fourth fraction which contained 0.19 g (62% based on unrecovered starting material) of 3-(2-methyl-5-hydroxyphenyl)propanal (**20**), and a fifth fraction which contained 0.07 g (8%, based on unrecovered starting material) of 5/6-fused acetoxy ketone **14**.

Irradiation of (1*S*,7a*S*)-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-5(7a*H*)-indanone (1a) in Aqueous Acetic Acid. A solution of 4.52 g (11.25 mmol) of dienone **1a** containing 27% of the unoxidized 6/5-fused enone **5g** in 225 mL of THF was placed in a 600-mL capacity cylindrical glass vessel and agitated with a stream of prepurified N_2 while 225 mL of water was added slowly. To the turbid mixture was added 30 mL of glacial acetic acid. The resulting clear solution was irradiated with a 450-W high-pressure mercury lamp housed in a Pyrex probe for 2.0 h. After this period, the starting material had disappeared as evidenced by TLC analysis (25% ethyl acetate in hexane) of an aliquot of the solution. The reaction mixture was then poured into 100 mL of ether, the organic layer was separated, and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ (5 × 50 mL) and then with 75 mL of brine. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give 5.83 g of a mixture of photoproducts. Subjection of the mixture to flash column chromatography (20–30% ethyl acetate in hexane) gave as an initial fraction 1.24 g of unoxidized 6/5-fused enone **5g**. Further elution of the column gave a second fraction which contained 0.06 g (4%) of (2-methyl-5-hydroxyphenyl)-propanal (**20**), a third fraction which contained 0.16 g (5%, based on unrecovered starting material) of 5/6-fused acetoxy ketone **2a**, a fourth fraction which contained 1.50 g (47% based on unrecovered starting material) of 5/6-fused hydroxy ketone **21** [^{1}H NMR (360 MHz) δ 1.07 (s, 3 H), 1.09 (s, 9 H), 1.49 (m, 1 H), 1.78 (m, 1 H), 2.07 (m, 1 H), 2.40 (m, 3 H), 2.60 (m, 1 H), 2.74 (d, J = 6 Hz, 1 H), 3.83 (dd, J = 4.6, 11.7 Hz, 1 H), 5.82 (s, 1 H), 7.42 (m, 6 H), 7.71 (m, 4 H); ^{13}C NMR (360 MHz) δ 14.52, 19.38, 26.99, 27.16, 27.69, 30.45, 36.39, 50.05, 78.51, 127.61, 127.68, 128.66, 129.92, 133.69, 135.82, 179.04, 209.50; IR ($CDCl_3$) 3560, 2950, 2930, 2860, 1705, 1630 cm^{-1}; HRMS m/z calcd for $C_{22}H_{23}O_3Si$ (M – C_4H_9 (*tert*-butyl)) 363.1417, obsd 363.1397], and a fifth fraction which contained 0.50 g (15% based on unrecovered starting material) of the cyclopropyl ketone **22**: ^{1}H NMR (360 MHz) δ 1.00 (s, 3 H), 1.04 (s, 9 H), 1.18 (m, 2 H), 1.52 (m, 2 H), 1.71 (m, 1 H), 1.90 (d, J = 5.5 Hz, 1 H), 2.12 (d, J = 5.5 Hz, 1 H), 2.51 (d, J = 17 Hz, 1 H), 2.77 (d, J = 17 Hz, 1 H), 4.07 (dd, J = 7.5, 10 Hz, 1 H), 7.40 (m, 6 H), 7.72 (m, 4 H); ^{13}C NMR (360 MHz) δ 19.34, 25.68, 26.87, 29.69, 35.79, 36.34, 43.05, 45.39, 58.33, 72.48, 73.00, 127.46, 127.55, 129.59, 129.63, 133.70, 134.02, 135.90, 209.10; IR ($CDCl_3$) 3590, 2960, 2940, 2860, 1720 cm^{-1}; HRMS m/z calcd for $C_{22}H_{23}O_3Si$ (M – C_4H_9 (*tert*-butyl)), 363.1417, obsd 363.1418.

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Supplementary Material Available: ^{1}H and in some cases ^{13}C NMR spectra for all relevant compounds (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis of Four Stereoisomeric Tetrose Derivatives from Propargyl Alcohol. One-Carbon Homologation of Vinylsilanes via α,β-Epoxy Silanes

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Silicon-mediated synthesis of stereoisomeric tetroses **1**, **2**, **3**, and **4**, from propargyl alcohol, is described. An allylic alcohol bearing the trimethylsilyl group in the γ-position, *rac*-**9b**, was subjected to the Sharpless kinetic resolution to give (2*S*)-**9b** and the (2*S*,3*S*,4*S*)-epoxide **10a** of very high enantiomeric purity (≥97% ee). Compound (2*S*)-**9b** was epoxidized with *tert*-butyl hydroperoxide and vanadyl acetylacetonate to give epoxide **14a** as the major product. Epoxy silanes **10a** and **14a** were treated with benzenethiol in the presence of silica gel to give the corresponding sulfides (**11a** and **16a**). Sulfides **11b** and **16b** were oxidized to sulfoxides which, without isolation, were subjected to the Pummerer rearrangement followed by hydrolysis. Intermediate vinylsilane **9a** was prepared from vinylsilane **6** via epoxy silane **7** using a novel homologation method.

A general method of carbohydrate synthesis has recently been developed[1] on the basis of titanium-mediated asymmetric epoxidation of allylic alcohols[2] and stereoselective transformations of hydroxy epoxides. Although the success

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