Synthesis and Photochemical Rearrangements of Bicyclic Cross-Conjugated Cyclohexadienones Containing δ-Oxy Substituents

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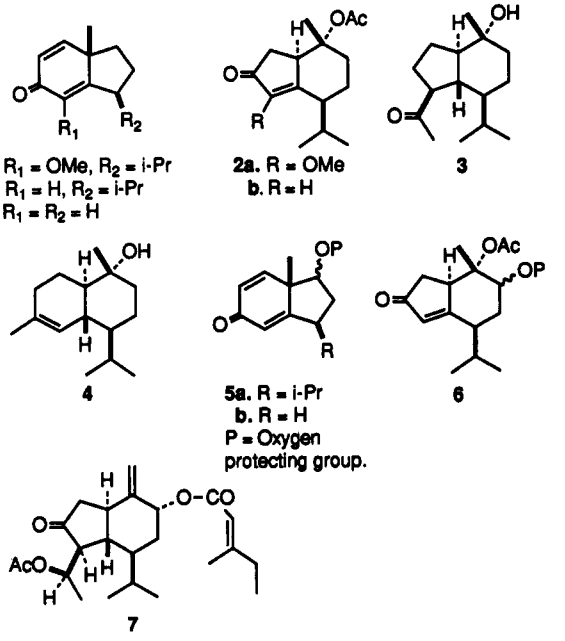
Received April 30, 1991

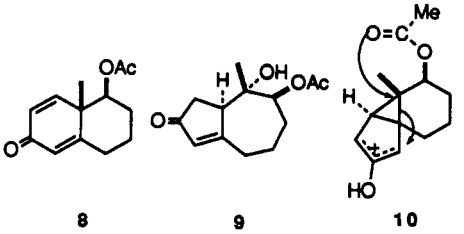
Several 6/5-fused cross-conjugated cyclohexadienones containing δ-oxy substituents on the B ring including the benzoyl, SEM, and TBDPS hydroxyl-protected systems **12b**, **12f**, and **12g** were prepared from the corresponding enones by the phenylselenenylation–selenoxide elimination procedure. Attempted preparation of dienones **12a**, **12c**, and **12d** containing *tert*-butyl, methyl, and trimethylsilyl hydroxyl-protecting groups failed. Instead, the phenolic aldehyde **13** was obtained after workup or column chromatography on silica gel. The THP-protected dienone **12e** could be purified and characterized, but it gave aldehyde **13** on standing in acetic acid at room temperature. Irradiations of dienones **12b**, **12f**, and **12g** in glacial acetic acid using a high-pressure mercury lamp housed in a Pyrex probe gave mixtures containing several photoproducts. The corresponding 5/6-fused acetoxy ketones **22a**, **22c**, and **22b** were the major products in each case. The 5/6-fused hydroxy ketone **23** was also obtained from dienone **22a**. Mixtures of tricyclic ketones of the type **27** and **28** resulting from rare examples of trapping of Zimmerman–Schuster cyclopropyl carbocation intermediates, i.e., **26**, by the solvent were also obtained from all three dienones. Dienones **12g** and **12f** also gave tricyclic acetoxy ketones **31a** and **31b**, which presumably arose via a 1,4-sigmatropic rearrangement of an excited-state precursor of **26**.

Introduction

Bicyclic cross-conjugated cyclohexadienones are well-known to undergo interesting acid-catalyzed (dienone–phenol)[1] and photochemical rearrangements.[2] The latter reactions may lead to a variety of complex ring systems and have served as key steps for the total synthesis of several fused-ring and spirocyclic naturally occurring sesquiterpenes.[3] For example, irradiation of 6/5-fused dienones such as **1a** and **1b** in glacial acetic acid yielded the corresponding 5/6-fused acetoxy enones **2a** and **2b**, which were converted into (±)-oplopanone (**3**)[4] and (±)-α-cadinol (**4**),[5] respectively. An analogous rearrangement of a 6/5-fused dienone such as **5a**, which contains an oxy substituent on the B ring at the δ position with respect to the carbonyl group, should provide a 5/6-fused photoproduct such as **6**, which is a potential precursor to the highly oxygenated oplopane derivative tussilagone (**7**). Tussilagone was isolated from the flowers of the Chinese herb *Tussilago farfara* L., and its structure and absolute configuration were established by spectroscopic methods and X-ray crystallography.[6] The natural product has been shown to have potent cardiovascular–respiratory activity in laboratory animal tests.[7]



Sometime ago we found that the 6/6-fused δ-acetoxy dienone **8** underwent photochemical rearrangement to give largely the 5/7-fused enone **9** upon irradiation in aqueous acetic acid.[8] This result was of interest since it had been shown earlier by Kropp and Erman that related ring-A unsubstituted dienones containing no δ substituents yield approximately equal amounts of 5/7-fused and spirocyclic hydroxy enones as well as phenols under similar conditions.[2,9] The behavior of dienone **8** is possibly attributable to participation of the acetoxy group in the selective cleavage of the internal bond of the cyclopropane ring in the carbocation intermediate **10**, which arises by the pathway proposed by Zimmerman and Schuster.[2,10]



Before undertaking the total synthesis of tussilagone, it appeared advisable to synthesize and investigate the photochemistry of model 6/5-fused dienones such as **5b** containing ester- or ether-type protecting groups on the

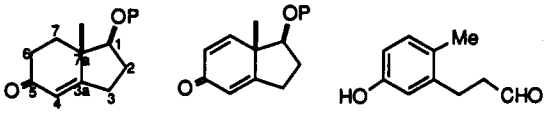
(1) Waring, A. J.; Zaidi, J. H.; Pilkington, J. W. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1454, and references cited therein.
(2) For reviews, see: (a) Kropp, P. *J. Org. Photochem.* **1967**, *1*, 1. (b) Schaffner, K. *Adv. Photochem.* **1966**, *4*, 81. (c) Schaffner, K. *Organic Reactions in Steroid Synthesis*; Fried, J., Edwards, J. A., Ed.; Van Nostrand-Reinhold: New York, 1972; Vol. II, pp 330–338. (d) Schuster, D. I. *Acc. Chem. Res.* **1978**, *11*, 65.
(3) (a) Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Plavac, F.; White, C. T. *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; John Wiley and Sons: New York, 1983; Vol. 5. (b) *Carbocycle Construction in Terpene Synthesis*; Ho, T. L., Ed.; VHC Publishers: New York, 1988; pp 105–106, 588–590, 630–631.
(4) Caine, D.; Tuller, F. N. *J. Org. Chem.* **1973**, *38*, 3663.
(5) Caine, D.; Frobese, A. S. *Tetrahedron Lett.* **1977**, 3107.
(6) Ying, B. P.; Yang, P. M.; Zhu, R. H. *Acta. Chim. Sinica* **1987**, *45*, 450; *Chem Abstr.* **1987**, *107*, 102504n.
(7) Li, Y.; Wang, Y. *Gen. Pharm.* **1988**, *19*, 261.
(8) Caine, D.; Tuller, N. F.; Doolittle, A. Unpublished work. See ref 2a, p 11.
(9) Kropp, P. J.; Erman, W. F. *J. Am. Chem. Soc.* **1963**, *85*, 2456.
(10) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527.

0022-3263/91/1956-6307$02.50/0

B-ring oxygen atom. Herein we report the results of this study.

Results and Discussion

Synthesis of Dienones. Initially, we attempted to convert the known chiral 6/5-fused *tert*-butoxy enone **11b**[11] into the cross-conjugated dienone **12a**. When **11b** was subjected to the phenylselenenylation–selenoxide elimination procedure,[12] which we[5,13] and others[14] have used successfully for several related transformations, the only product isolated after chromatography of the crude reaction mixture on silica gel was the propanal derivative **13** in 38% yield. Likewise, attempted oxidation of **11b** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene gave only the aldehyde **13** and none of the expected dienone. In contrast, subjection of the benzoyloxy enone **11c**, prepared from the corresponding hydroxy enone **11a**,[15] to the phenylselenenylation–selenoxide elimination procedure yielded dienone **12b** in 70% yield.



11a. P = H
b. P = t-butyl
c. P = OCPh
d. P = Me
e. P = TMS
f. P = THP
g. P = SEM
h. P = TBDPS

12a. P = t-butyl
b. P = OCPh
c. P = Me
d. P = TMS
e. P = THP
f. P = SEM
g. P = TBDPS

13

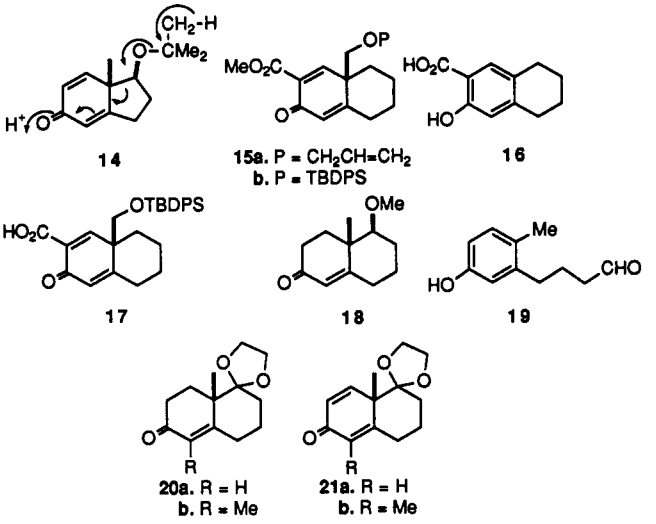
It appeared that the aldehyde **13** was formed by way of the unstable dienone intermediate **12a**. The instability of the dienone could result from the fact that a facile cleavage of the γ,δ carbon–carbon bond could occur via the pathway depicted in structure **14**. A similar cleavage pathway would not be available to dienone **12b** where a benzoyl rather than a *tert*-butyl group is present on the δ oxygen atom.

In an effort to determine what kinds of oxygen-protecting groups might impart stability to dienone systems of the type **12**, several protected enones (cf. **11**) were prepared and subjected to the phenylselenenylation–selenoxide elimination procedure. As was the case for the *tert*-butoxy dienone **12a**, the corresponding methoxy **12c** and trimethylsiloxy dienones **12d** were too unstable to be isolated. Only the propanal derivative **13** was obtained in approximately 35–40% yield in each case after chromatography of the reaction mixture on silica gel.

The dienone **12e** containing a tetrahydropyranyl (THP) protecting group was produced from the corresponding known enone **11f**[16] and was sufficiently stable to be purified as described above. However, in a separate experiment it was found that **12e** was completely converted into the aldehyde **13** upon standing in glacial acetic acid solution at room temperature for 45 min.

The [β-(trimethylsilyl)ethoxy]methyl (SEM),[16] and *tert*-butyldiphenylsilyl (TBDPS) protected enones **11g** and **11h** were converted into the corresponding dienones **12f** and **12g** in 93% and 99% yields (based on recovered starting material), respectively. Also, solutions of these dienones in glacial acetic acid were stable at room temperature for 45 min.

The above results show that the structure and electronic nature of the protecting group can have a profound affect on the stability of dienones of the type **12**. Apparently, if the group attached to the δ oxygen atom has an electron-withdrawing effect, the rate of cleavage of the γ,δ carbon–carbon bond is significantly retarded. Thus, dienones such as **12b**, which contain a benzoyl group bonded to oxygen, dienones such as **12e** and **12f**, which contain electronegative oxygen atoms in the protecting-group moiety, and dienone **12g**, which contains phenyl groups in the protecting-group moiety, are relatively stable. If such groups are not present as is the case for dienones **12a**, **12c**, and **12d** having *tert*-butyl, methyl, and trimethylsilyl substituents on the δ oxygen atom, acid-promoted cleavage of the γ,δ bond with concerted or subsequent attack by water can yield a hemiacetal intermediate that is readily converted into aldehyde **13**. This suggestion was reinforced by the fact that the hemiacetal acetate **34** was obtained when dienone **12f** was irradiated in glacial acetic acid for an extended time period (vide infra). The THP-protected dienone **12e** is capable of undergoing a concerted fragmentation of the type illustrated in structure **14**. Perhaps this accounts for its instability in acetic acid solution even though an oxygen atom is present in the protecting group moiety.



14

15a. P = $CH_2CH{=}CH_2$
b. P = TBDPS

16

17

18

19

20a. R = H
b. R = Me

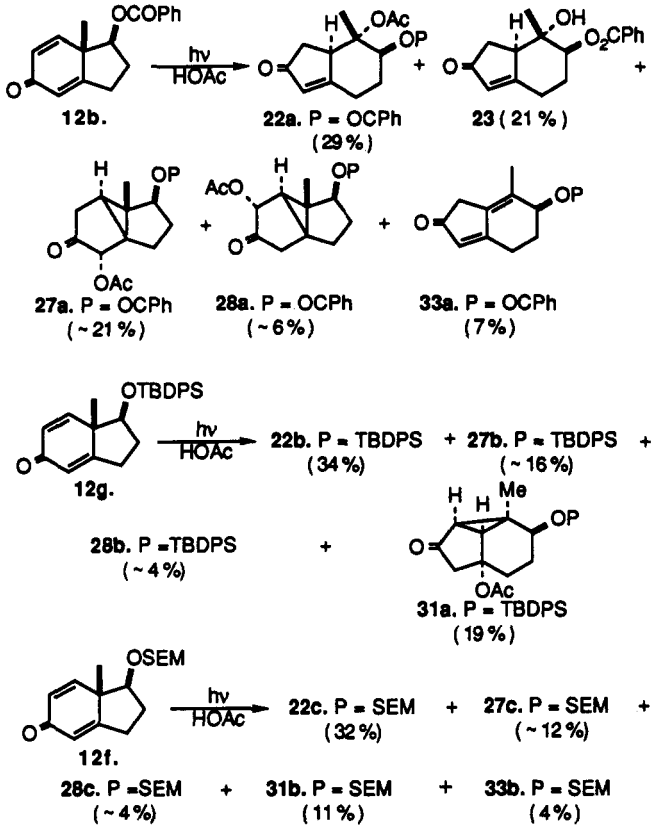
21a. R = H
b. R = Me

Another case in which the electronic nature of the protecting group in a δ-oxy substituent influenced the stability of a dienone system has been reported by Broka.[14b] Thus, attempted hydrolysis of the dienone ester **15a**, which contains an allyl group on oxygen, led exclusively to the phenol derivative **16** resulting from cleavage of the γ,δ carbon–carbon bond, but under the same conditions, the TBDPS-protected dienone **15b** gave the corresponding dienone acid **17**, cleanly.

In order to compare the behavior of a 6/6-fused dienone with the corresponding 6/5-fused system, the known δ-methoxy enone **18**[18] was subjected to the phenylselenenylation–selenoxide elimination procedure. As was the case for enone **11d**, cleavage of the B ring occurred and

(11) 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**, *40*, 675.
(12) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.
(13) (a) Caine, D., Boucugnani, A. A.; Pennington, W. R. *J. Org. Chem.* **1976**, *41*, 3632. (b) Caine, D.; Deutsch, H.; Gupton, J. T., III. *Ibid.* **1978**, *43*, 343.
(14) (a) Barton, D. H. R.; Lester, D. J.; Ley, S. U. *J. Chem. Soc., Chem. Commun.* **1978**, 130. (b) Broka, C. A. *J. Org. Chem.* **1988**, *53*, 575.
(15) Ruel, R.; Deslongchamps, P. *Tetrahedron Lett.* **1990**, *28*, 3961.
(16) Hajos, Z. G.; Parrish,. D. R.; Oliveto, E. P. *Tetrahedron* **1968**, *24*, 2039.
(17) Paquette, L. A.; Sugimara, T. *J. Am. Chem. Soc.* **1986**, *108*, 3841.
(18) Kim, M.; Kawada, K.; Watt, D. S. *Synth. Commun.* **1989**, *19*, 2017.

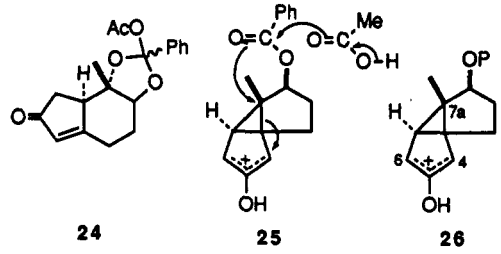
Scheme I



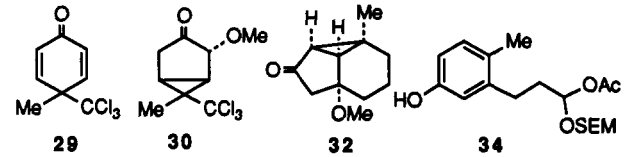
the only product isolated was the butanal derivative **19**. Also, an attempt to prepare dienone **21a** from the known enone ketal **20a**[19] by a similar procedure yielded a complex mixture from which none of the desired dienone could be isolated. It has been reported previously that attempted dehydrogenation of the related enone ketal **20b** with thallium(III) acetate yielded none of the expected dienone **21b**, but rather an aromatized product was apparently obtained.[20]

Photolysis of Dienones. The photochemical behavior of the three stable dienones **12b**, **12f**, and **12g** was next investigated. In each case, irradiation of a glacial acetic acid solution was carried out using a 450-W high-pressure mercury lamp housed in a water-cooled Pyrex probe. The irradiation times were 1.0 h for dienones **12b** and **12g** and 2.5 h for dienone **12f**. The structures and yields of the photoproducts are shown in Scheme I.

All three dienones gave the expected 5/6-fused acetoxy enones as the major products. In the case of the benzoyl-protected dienone **12b**, the 5/6-fused acetoxy enone **22a** and the 5/6-fused hydroxy enone **23** were obtained in 29% and 21% yields, respectively. The reason the hydroxy enone **23** was formed in the irradiation of **12b** is unclear. It possibly arose from hydrolysis of the ortho acetate **24** during aqueous workup or chromatography. Ortho acetate **24** may arise via the neighboring-group participation of the benzoyloxy substituent in the cleavage of the internal bond of the cyclopropane ring in the Zimmerman–Schuster intermediate, cf. **25**. In contrast, the SEM-protected dienone **12f** and the TBDPS-protected dienone **12g**, where neighboring-group participation of the substituent is unlikely, gave only the 5/6-fused acetoxy enones **22c** and **22b**, resulting from cleavage of the internal bond of the cyclopropane ring of the Zimmerman–Schuster intermediate **26** by acetic acid, in 32% and 34% yields, respectively. As was the case for the 6/5-fused dienones, **1b**[5] and **1c**,[22] no spirocyclic products derived from β solvent attack and cleavage of the external bond of the cyclopropane ring of intermediate **26** were observed.



Irradiations of each of the three dienones led to a mixture of tricyclic acetoxy ketones **27a–c** and **28a–c** derived from trapping of the Zimmerman–Schuster cyclopropyl carbocation intermediate **26** by acetic acid. None of the mixtures was separable by column chromatography or by preparative thin-layer chromatography, but the product ratios were determined by integration of the NMR absorptions of the C-4 and C-6 protons. These were clearly visible in each of the pairs of isomers at high resolution. The structural assignments of these photoproducts including the α configurations to the acetoxy groups at C-4 and C-6 were confirmed by NOE, 2D COSY, and HETCOR (heteronuclear correlation spectroscopy) experiments. In particular, NOE enhancements of both the C-4 and C-6 protons were observed when the 7a-methyl groups were irradiated in all three cases. Examination of models clearly reveals that solvent attack from the α side of the intermediate **26** is preferred because β attack is hindered by the 7a-methyl group. However, the reason that C-4 attack is favored somewhat over C-6 attack is unclear. Products of the type **27** and **28** provide the first examples of solvent trapping of Zimmerman–Schuster intermediates during photolysis of fused-ring cross-conjugated cyclohexadienones. This type of reaction has been reported by Schuster and co-workers[2d,21] who found that the monocyclic dienone 4-methyl-4-(trichloromethyl)cyclohexa-2,5-dienone (**29**) gave the bicyclic ketone **30** upon irradiation in methanol acidified with hydrogen chloride.



In previous studies on the photolysis of 6/5-fused dienones such as **1b** and **1c**, which do not contain δ oxygen substituents,[5,22] products of the type **27** or **28** were not isolated. Therefore, in dienones such as **12**, it appears that the β substituents reduce the rate of cleavage of the cyclopropane ring of the Zimmerman–Schuster intermediate **26** sufficiently to permit the trapping process to occur. This effect may be steric or electronic in origin. Clearly, the bulky substituent at C-1 in **26** could reduce the rate of solvent attack at C-7a; but also, the electron-withdrawing effect of the oxy substituent may destabilize the transition state for opening of the cyclopropane ring by

(19) Bauduin, G.; Pietra Santra, Y. *Tetrahedron* **1973**, *29*, 4225.
(20) Banerjee, A. K.; Carrasco, M. C.; Pena-Matheud, C. A. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 94.
(21) (a) Schuster, D. I.; Abraitys, V. Y. *J. Chem. Soc., Chem. Commun.* **1969**, 419. (b) See, also: Patel, D. J.; Schuster, D. I. *J. Am. Chem. Soc.* **1968**, *90*, 5137. Schuster, D. I.; Patel, D. J. *Ibid.* **1968**, *90*, 5145. Schuster, D. I.; Liu, K. C. *Tetrahedron* **1981**, *37*, 3329.
(22) Caine, D.; Gupton, J. T., III; Ming, K.; Powers, W. J., III. *J. Chem. Soc., Chem. Commun.* **1973**, 469.

increasing the amount of positive charge at C-7a.[23]

Irradiations of dienones **12g** and **12f** also gave tricyclic acetoxy ketones **31a** and **31b** in 19% and 11% yields, respectively. The structures of these compounds were established by NMR spectroscopy, including spin–spin decoupling, NOE, and HETCOR experiments. These products have analogous structures to the tricyclic methoxy ketone **32**, which was isolated previously from the irradiation of dienone **1c** in methanolic acetic acid.[22] As was proposed earlier for the formation of **32**,[22] compounds such as **31** may arise via electronic excitation and β,β-bonding of the dienone to produce a triplet-excited-state intermediate. Prior to electron demotion and protonation to give intermediate **26**, this species may undergo a symmetry-allowed 1,4-sigmatropic shift of C-7a from C-3a to C-6 with retention of configuration to give a strained tricyclic enone. Relief of strain by 1,4-addition of acetic acid to this species would yield **31**. It is not clear why irradiation of dienone **12b** did not yield a tricyclic ketone analogous to **31a** and **31b**. Perhaps the presence of the benzoyloxy group facilitates rapid conversion of the excited-state cyclopropyl intermediate to the ground state.

Finally, a 7% yield of the linearly conjugated 5/6-fused dienone **33a** was isolated from the photolysis of **12b**. A product, presumably **33b**, that was not conclusively identified but had similar spectral properties to those of **33a** was also isolated in ca. 4% yield from irradiation of dienone **12f**. These dienones are probably produced from loss of acetic acid or water from enones **22a** or **23** or loss of acetic acid from **22c** during chromatography on silica gel.

Somewhat lower yields of the various photoproducts were observed from irradiation of the SEM-protected dienone **11g**. This resulted from the fact that a relatively long irradiation period was required to complete the reaction. Thus, during this time the dienone underwent partial thermal reaction with acetic acid, which led to cleavage of the γ,δ carbon–carbon bond. The hemiacetal acetate **34** and the aldehyde **13** were isolated in 16% and 18% yields, respectively, from this reaction.

Conclusion

It was found that δ-oxy-substituted 6/5-fused dienones containing ester and certain ether protecting groups may be prepared and photochemically rearranged in glacial acetic acid. Although mixtures were obtained in each case, the major products were 5/6-fused enones of the type **22**. Therefore, a compound such as **5a** containing a β-isopropyl group at C-3 may serve as a useful precursor to the natural product tussilagone (**7**). All three of the dienones gave photoproducts derived from the trapping of Zimmerman–Schuster cyclopropyl intermediates (cf. **26**) by the solvent. These are the first cases in which such products have been isolated from irradiations of bicyclic dienones. Also, products derived from 1,4-sigmatropic rearrangements of excited-state precursors of **26**, which have been rarely observed previously, were obtained from dienones **12f** and **12g**.

(23) (a) On irradiation in aprotic solvents, e.g., dioxane most cross-conjugated cyclohexadienones, including 6/5-fused systems such as **1c**,[23b] are converted into bicyclo[3.1.0]hexenone derivatives (lumiproducts) via symmetry-allowed 1,4-sigmatropic rearrangements of zwitterionic intermediates.[2,10] In some cases, e.g., dienone **29**, there is competition between lumiproduct formations and other reactions of zwitterionic species or their conjugate acids.[21] However, neither lumiproducts nor secondary products derived from their further photochemical or thermal reactions were obtained in previously conducted irradiations of dienones such as **1**[4,5,22] in protic media or in the present work in which dienones **12b**, **12f**, and **12g** were irradiated in glacial acetic acid. (b) Caine, D.; Alejande, A. M.; Ming, K.; Powers, W. J., III. *J. Org. Chem.* **1972**, *37*, 706.

Experimental Section

General. Benzoyl chloride, dihydropyran, [β-(trimethylsilyl)ethoxy]methyl chloride, *tert*-butyldiphenylsilyl chloride, diphenyl diselenide, sodium hydride, bromine, and imidazole were purchased from Aldrich Chemical Co. or Fisher Scientific Co. and used without further purification. Methyl iodide was purified by passing it through a small column of silica gel. Methylene chloride, dimethylformamide (DMF), diisopropylamine, triethylamine, and trimethylsilyl chloride were distilled over calcium hydride prior to use. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium/benzophenone ketyl. Acetic anhydride was distilled over phosphorus pentoxide and acetic acid was freshly distilled prior to use.

^{1}H NMR and ^{13}C NMR spectra were recorded on 200-, 360-, or 500-MHz spectrometers ($CDCl_3$ solvent, TMS internal standard). Infrared (IR) spectra were recorded in $CHCl_3$ solution using NaCl solution cells. Mass spectra (MS) were obtained using electron-impact ionization or chemical ionization. Reaction products were purified by flash column chromatography using silica gel (support-grade catalyst 951) purchased from Aldrich Chemical Company. Analytical samples were prepared by preparative thin-layer chromatography 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 magnesium sulfate, and the solvents were removed in vacuo using a rotary evaporator operated at water aspirator pressure.

(1(*S*),7a(*S*))-1-Methoxy-7a-methyl-7,7a-dihydro-5(6*H*)-indanone (11d). To 0.166 g (1.0 mmol) of (+)-(1(*S*),7a(*S*))-7a-methyl-7,7a-dihydro-1-hydroxy-5(6*H*)-indanone (**11a**) in 4.0 mL of DMF was added 3.1 mL (50 mmol) of methyl iodide at 25 °C. The mixture was cooled to −20 °C, and 0.072 g (3 mmol) of a slurry of sodium hydride (washed three times with hexane to remove oil) in 4.0 mL DMF was added. The reaction mixture was stirred for 30 min at −20 °C and quenched with methanol. The mixture was poured into 5 mL of water, concentrated to half its original volume, and extracted with 2 × 10 mL of ethyl acetate. The organic layer was washed with 2 × 10 mL of water and 2 × 10 mL of brine and dried, and the solvent was removed in vacuo. Purification by flash column chromatography (20% ethyl acetate in hexane) gave 0.15 g (83%) of **11d**: ^{1}H NMR (200 MHz) δ 1.14 (s, 3 H), 1.81 (m, 2 H), 2.33 (m, 5 H), 2.72 (m, 1 H), 3.41 (m, 4 H), 5.77 (s, 1 H); ^{13}C NMR (360 MHz) δ, 15.70, 26.22, 26.46, 33.35, 35.09, 45.15, 58.02, 89.31, 123.20, 174.84, 199.00; IR ($CHCl_3$) 3000, 2960, 1661, 1370, 1340, 1200, 1105 cm^{-1}; high-resolution MS m/z calcd for $C_{11}H_{16}O_2$ (M^+) 180.1150, obsd 180.1152.

(1(*S*),7a(*S*))-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-7,7a-dihydro-5(6*H*)-indanone (11h). To 1.2 g (7.23 mmol) of **11a** in 12 mL of methylene chloride was added imidazole, 1.48 g (21.7 mmol), and *tert*-butyldiphenylsilyl chloride, 2.07 mL (7.95 mmol). The solution was stirred at room temperature for 24 h. The reaction mixture was washed with 10 mL of cold 10% HCl to remove the excess imidazole. The organic layer was then washed with saturated aqueous $NaHCO_3$ (2 × 10 mL) and brine (10 mL). The combined organic layers were dried and filtered and the solvent removed in vacuo to give 3.12 g of a crude pale yellow oil. Flash column chromatography (20% ethyl acetate in hexane) of the product and further purification by Kugelrohr distillation at 180 °C (0.005 Torr) gave 2.56 g (87%) of **11h**: ^{1}H NMR (500 MHz) δ 1.09 (s, 9 H), 1.25 (s, 3 H), 1.45 (m, 1 H), 1.70 (m, 1 H), 1.84 (m, 1 H), 1.98 (m, 1 H), 2.22 (m, 2 H), 2.47 (m, 1 H), 2.59 (m, 1 H), 3.76 (d of d, J = 7.5, 10.0 Hz, 1 H), 5.68 (s, 1 H), 7.38 (m, 4 H), 7.44 (m, 2 H), 7.66 (m, 4 H); ^{13}C NMR (500 MHz) δ, 15.67, 19.32, 26.52, 27.00, 29.35, 33.37, 34.18, 45.90, 81.37, 123.25, 127.75, 129.82, 133.75, 135.86, 174.41, 199.20; IR ($CHCl_3$) 3150, 3080, 2980, 2970, 1660, 1470, 1425, 1380, 1140, 1100, 900 cm^{-1}; high resolution MS (chemical ionization) m/z calcd for $C_{26}H_{33}O_2Si$ (M + 1) 405.2250, obsd 405.2222.

(1(*S*),7a(*S*))-1-(Trimethylsiloxy)-7a-methyl-7,7a-dihydro-5(6*H*)-indanone (11e). To 1.66 g (10 mmol) of **11a** in 15 mL of methylene chloride was added imidazole, 2.04 g (30 mmol), and freshly distilled trimethylsilyl chloride, 1.5 mL (12.5

mmol). The solution was stirred at room temperature for 24 h. The reaction mixture was washed with 10 mL of cold 5% HCl followed by saturated aqueous $NaHCO_3$ (2 × 10 mL) and brine (10 mL). The combined organic layers were dried and filtered and the solvent was removed in vacuo to give 2.36 g of a crude yellow oil. Purification by flash column chromatography (15% ethyl acetate in hexane) gave 1.67 g (70%) of **11e**: ^1H NMR (500 MHz) δ, 0.11 (s, 9 H), 1.09 (s, 3 H), 1.69 (m, 1 H), 1.80 (m, 1 H), 1.97 (m, 2 H), 2.36 (m, 2 H), 2.50 (m, 1 H), 2.68 (m, 1 H), 3.73 (d of d, J = 7.5, 10 Hz, 1 H), 5.76 (s, 1 H); ^{13}C NMR (500 MHz) δ, 0.10, 15.19, 26.51, 29.52, 33.36, 34.29, 45.35, 80.60, 123.29, 175.05, 199.26; IR ($CHCl_3$) 2995, 2950, 1661, 1415, 1370, 1340, 1250, 1200, 1140, 1100 cm^{-1}; high-resolution MS m/z calcd for $C_{13}H_{22}O_2Si$ (M^+) 238.1389, obsd 238.1366.

General Procedure for Conversions of Enones 11c,f,g,h to the Corresponding Dienones 12b,e,f,g. To 2.1 mmol of a solution of LDA in 5 mL of THF at −78 °C was added dropwise with stirring 1.0 mmol of the hydroxyl-protected enone **11b–h** in 5 mL of THF over a period of 15 min. The solution was stirred for 45 min at −78 °C. A freshly prepared solution of 1.2 mmol phenylselenyl bromide in 5 mL of THF was added all at once at −78 °C and the reaction mixture stirred at that temperature for 2 h. The reaction mixture was allowed to warm to room temperature and quenched by addition of 5 mL of cold saturated aqueous NH_4Cl. The aqueous layer was extracted twice with ether (10 mL), and the combined organic layers were then washed with brine (10 mL), dried ($MgSO_4$), and filtered. The solvent was then removed under reduced pressure to give a dark brown residue of the crude 6-phenylselenenyl derivative of the enone. After purification by flash chromatography on silica gel (10–15% ethyl acetate hexane), the enone derivative was dissolved in 10 mL of ethyl acetate, the solution was cooled to 20 °C, and 0.34 mL (3 mmol) of H_2O_2 (30%) diluted with 1.0 mL water was added dropwise with stirring over 10 min, and stirring was continued for 2–3 h at 20 °C. 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 under reduced pressure gave the dienone as pale yellow oil that was purified by flash column chromatography (10–25% ethyl acetate in hexane) on silica gel that had been neutralized with 5% triethylamine in hexane.

(1(*S*),7a(*S*))-1-(Benzoyloxy)-7a-methyl-5(7a*H*)-indanone (12b). Treatment of 2.7 g (10 mmol) of **11c** in the manner described above gave 0.82 g (31%) of recovered starting enone **11c** and 2.71 g (92%, based on unrecovered starting material) of the 6-phenylselenenyl derivative of enone **11c**: ^1H NMR (200 MHz) δ, 1.2 (s, 3 H), 1.65–2.9 (br abs, 6 H), 4.20 (d of d, J = 5, 14 Hz, 1 H), 5.22 (t, J = 8.5 Hz, 1 H), 5.91 (s, 1 H), 7.3–8.18 (br abs, 10 H).

Oxidation of 2.44 g of this compound in the manner described above gave after workup and purification 1.05 g (70%) of dienone **12b**: ^1H NMR (360 MHz) δ 1.41 (s, 3 H), 2.13 (m, 1 H), 2.57 (m, 2 H), 2.99 (m, 1 H), 5.14 (t, J = 8.6 Hz, 1 H), 6.16 (br s, 1 H), 6.24 (d of d, J = 10, 1.5 Hz, 1 H), 7.08 (d, J = 10 Hz, 1 H), 7.49 (m, 2 H), 7.62 (m, 1 H), 8.06 (m, 2 H); ^{13}C NMR (360 MHz) δ 20.43, 26.64, 27.75, 48.46, 75.97, 124.50, 128.57, 129.64, 129.71, 133.42, 150.69, 165, 168, 186; IR ($CHCl_3$) 3150, 3000, 2875, 1730, 1672, 1645, 1611, 1460, 1400, 1380, 1320, 1300, 1275, 1220, 1210, 1110, 1090 cm^{-1}; high-resolution MS m/z calcd for $C_{17}H_{16}O_3$ (M^+) 268.1094, obsd 268.1100.

(1(*S*),7a(*S*))-1-(Tetrahydropyranyloxy)-7a-methyl-5-(7a*H*)-indanone (12e). Treatment of 2.0 g (8.0 mmol) of **11f** in the general manner described for the preparation of the dienones gave 0.36 g (18%) of recovered starting material **11f** and 2.28 g (86%, based on unrecovered starting material) of the 6-phenylselenenyl derivative of **11f**: ^1H NMR (200 MHz) δ 1.13 (s, 3 H), 1.28 (m, 1 H), 1.43–2.24 (br abs, 10 H), 2.34 (m, 2 H), 2.69 (m, 1 H), 3.27–3.93 (br abs, 3 H), 4.29 (m, 1 H), 4.57 (m, 1 H), 5.85 (s, 1 H), 7.29 (m, 3 H), 7.61 (m, 2 H).

Oxidation of 1.87 g of phenylselenenyl derivative of **11f** in the manner described above gave 1.05 g (92%) of dienone **12e**: ^1H NMR (200 MHz) δ 1.2 (s, 3 H), 1.6–2.8 (br abs, 10 H), 3.47 (m, 1 H), 3.81 (m, 2 H), 4.60 (s, 1 H), 6.02 (s, 1 H), 6.16 (d of d, J = 10, 1.5 Hz, 1 H), 6.96 (d, J = 10 Hz, 0.5 H), 7.17 (d, J = 10 Hz, 0.5 H); IR ($CHCl_3$) 2940, 2860, 1665, 1635, 1600, 1495, 1445, 1380, 1120, 1070, 1030 cm^{-1}; high-resolution MS m/z calcd for $C_{15}H_{20}O_3$ (M^+) 248.1413, obsd 248.1406.

(1(*S*),7a(*S*))-1-[[β-(Trimethylsilyl)ethoxy]methoxy]-7a-methyl-5(7a*H*)-indanone (12f). Treatment of 4.66 g (15.75 mmol) of enone **11g** in the manner described above gave 1.48 g (32%) of recovered starting enone **11g** and 3.95 g (82%, based on unrecovered starting material) of 6-phenylselenenyl derivative of **11g**: ^1H NMR (200 MHz) δ 0.03 (s, 9 H), 0.87 (t, J = 8.5 Hz, 2 H), 1.13 (s, 3 H), 1.59–2.81 (br abs, 6 H), 3.60 (m, 3 H), 4.32 (d of d, J = 14, 5 Hz, 1 H), 4.64 (m, 2 H), 5.86 (s, 1 H), 7.28 (m, 3 H), 7.59 (m, 2 H).

Oxidation of 3.95 g of this compound in the manner described above gave 2.4 g (93%) of dienone **12f**: ^1H NMR (200 MHz) δ 0.03 (s, 9 H), 0.89 (J = 8.5 Hz, 2 H), 1.23 (s, 3 H), 1.97 (m, 1 H), 2.36 (m, 2 H), 2.82 (m, 1 H), 3.71 (m, 3 H), 4.72 (m, 2 H), 6.09 (d, J = 1.5 Hz, 1 H), 6.21 (d of d, J = 10, 1.5 Hz, 1 H), 7.11 (d, J = 10 Hz, 1 H); ^{13}C NMR (360 MHz) δ −1.46, 18.09, 19.35, 26.46, 28.39, 48.92, 65.42, 80.10, 94.77, 124.06, 128.40, 151.81, 170.54, 186.43; IR ($CHCl_3$) 2960, 1670, 1650, 1620, 1380, 1130, 1040 cm^{-1}; high-resolution MS m/z calcd for $C_{11}H_{13}O_3$ (M − $C_5H_{13}Si$) 193.0865, obsd 193.0879.

(1(*S*),7a(*S*))-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-5-(7a*H*)-indanone (12g). Treatment of 2.42 g (6 mmol) of **11h** in the manner described above gave 0.47 g (19%) of recovered starting material **11h** and 2.69 g (99%, based on unrecovered starting material) of the 6-phenylselenenyl derivative of **11h**: ^1H NMR (200 MHz) δ 0.98 (s, 9 H), 1.2 (s, 3 H), 1.77 (m, 3 H), 2.15 (m, 2 H), 2.58 (m, 1 H), 3.64 (d of d, J = 7.5, 10 Hz, 1 H), 4.27 (d of d, J = 14, 5 Hz, 1 H), 5.76 (s, 1 H), 7.27–7.62 (br abs, 15 H).

Oxidation of 2.69 g of this compound in the manner described above gave 1.71 g (99%) of dienone **12g**: ^1H NMR (360 MHz) δ 1.11 (s, 9 H), 1.31 (s, 3 H), 1.90 (m, 2 H), 2.24 (m, 1 H), 2.76 (m, 1 H), 3.91 (d of d, J = 7.5, 10 Hz, 1 H), 5.98 (d, J = 1.5 Hz, 1 H), 6.03 (d of d, J = 10, 1.5 Hz, 1 H), 6.82 (d, J = 10 Hz, 1 H), 7.65 (m, 4 H), 7.39 (m, 6 H); ^{13}C NMR (500 MHz) δ 19.08, 19.29, 26.53, 26.98, 30.67, 50.02, 75.84, 124.07, 127.63, 127.80, 127.98, 127.90, 135.77, 151.84, 170.52, 186.48; IR ($CHCl_3$) 3020, 3000, 2940, 2860, 1660, 1635, 1600, 1460, 1425, 1390, 1370, 1260, 1210, 1100 cm^{-1}; high-resolution MS m/z calcd for $C_{22}H_{21}O_2Si$ (M − C_4H_9) 345.1311, obsd 345.1293.

3-(2-Methyl-5-hydroxyphenyl)propanal (13). Treatment of 1.40 g (7.75 mmol) of enone **11d** in the manner described above gave 1.26 of an oil after workup. This material was purified by flash column chromatography (15% ethyl acetate in hexane) to give 0.47 g (38%) of aldehyde **13** as an oil. Aldehyde **13** was further purified by recrystallization from ether/hexane to give pale yellow crystals, mp 70–72 °C: ^1H NMR (200 MHz) δ 2.18 (s, 3 H), 2.80 (m, 4 H), 4.84–5.99 (br abs, 1 H), 6.67 (m, 2 H), 7.0 (d, J = 8 Hz, 1 H), 9.8 (s, 1 H); IR ($CHCl_3$) 3600, 2810, 2720, 1722, 1610, 1500, 1460, 1380, 900 cm^{-1}; high-resolution MS m/z calcd for $C_{10}H_{12}O_2$ (M^+) 164.0837, obsd 164.0836. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.12; H, 7.32. Found: C, 72.97; H, 7.32.

In a similar manner, oxidation of enones **11b** and **11e** also gave aldehyde **13** in 35–40% yield.

4-(2-Methyl-5-hydroxyphenyl)butanal (19). Treatment of 1.15 g (6 mmol) of enone **18** in the manner described for the preparation of the 6/5-fused dienones gave 0.13 g (11%) of recovered starting enone **18** and 1.59 g (86%, based on unrecovered starting material) of 6-phenylselenenyl derivative of **18**: ^1H NMR (200 MHz) δ 1.14 (s, 3 H), 1.37 (m, 2 H), 1.96 (m, 3 H), 2.27 (m, 2 H), 2.51 (d of d, J = 5, 13.5 Hz, 1 H) 2.82 (d of d, J = 11, 4 Hz, 1 H), 3.3 (s, 3 H), 4.23 (d of d, J = 14, 5 Hz, 1 H), 5.85 (s, 1 H), 7.28 (m, 3 H), 7.59 (m, 2 H).

Oxidation of 1.5 g of phenyl selenenyl derivative of **18** in the manner described above gave 0.29 g (36%) of aldehyde **19** as yellow oil: ^1H NMR (200 MHz) δ 1.75 (m, 2 H), 2.09 (s, 3 H), 2.40 (m, 4 H), 6.51 (m, 2 H), 6.86 (d, J = 8.8 Hz, 1 H), 9.61 (s, 1 H); IR ($CHCl_3$) 3500, 3020, 2880, 2740, 1720, 1600, 1500, 1450 cm^{-1}; high-resolution MS m/z calcd for $C_{11}H_{14}O_2$ (M^+) 178.0994, obsd 178.0978.

General Procedure for Irradiation of Dienones 12b, 12f, and 12g. A solution of 200 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 nitrogen for 5 min while being irradiated with a 450-W high-pressure mercury lamp housed in a water-cooled Pyrex probe. Then the dienone, diluted with a small volume of ether to permit easy transfer, was introduced via a canula. The solution was irradiated until the starting material disappeared as evidenced by TLC analysis of an aliquot. The solvent was then removed in vacuo finally at ~0.5 mm of pressure. The residue was dissolved in 25 mL of ether, and the solution was washed with 2 × 25 mL of saturated $NaHCO_3$ and then with 25 mL of brine. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give a mixture of the photoproducts, which was separated by flash chromatography on silica gel.

Irradiation of (1(*S*),7a(*S*))-1-(Benzoyloxy)-7a-methyl-5-(7a*H*)-indanone (12b). Irradiation of 0.91 g (3.4 mmol) of **12b** for 1.0 h followed by workup as described above gave 0.33 g (29%) of an inseparable mixture of tricyclic acetoxy ketones **26a** and **27a** in a 3.5:1 ratio as determined by NMR spectroscopy [^{1}H NMR (200 MHz) δ 1.02 (s, 3 H), 1.60 (d, J = 6.5 Hz, 1 H), 1.70 (m, 1 H), 1.84 (m, 2 H), 2.10 (s, 0.63 H, OAc in **28a**), 2.17 (s, 1.94 H, OAc in **27a**), 2.32 (m, 2 H), 2.40 (d, J = 19.9 Hz, 0.17 H, C-4H in **28a**), 2.81 (d of d, J = 20, 6.7 Hz, 0.70 H, C-6H in **27a**), 2.92 (d, J = 20 Hz, 0.17 H, C-4H in **28a**) 4.59 (s, 0.21 H, C-6H in **28a**), 4.72 (s, 0.71 H, C-4H in **27a**), 5.48 (d, J = 5 Hz, 1 H), 7.41 (m, 2 H), 7.56 (m, 1 H), 8.05 (m, 2 H); ^{13}C NMR (360 MHz) δ 7.10, 20.28, 22.32, 24.93, 28.05, 34.25, 36.47, 37.57, 73.79, 80.52, 128.36, 129.52, 130.25, 133.0, 165.8, 169.8, 213.7; IR ($CHCl_3$) 3040, 3020, 2990, 2980, 2950, 1765, 1750, 1720, 1610, 1455, 1375, 1280, 1230, 1100 cm^{-1}; high-resolution MS m/z calcd for $C_{17}H_{17}O_3$ (M - $C_2H_3O_2$ (OAc)) 269.1178 obsd 269.1135]; 0.06 g (6%) of the 5/6-fused linear dienone **33a** [^{1}H NMR (200 MHz) δ 1.91 (s, 3 H), 2.15 (m, 2 H), 2.78 (m, 2 H), 2.96 (s, 2 H), 5.73 (t, J = 4.7 Hz, 1 H), 5.99 (s, 1 H), 7.45 (m, 2 H), 7.58 (m, 1 H), 8.05 (m, 2 H); IR ($CHCl_3$) 3010, 1710, 1200 cm^{-1}; high-resolution MS m/z calcd for $C_{17}H_{16}O_3$ (M$^+$) 268.1100, obsd. 268.1084]; 0.32 g (29%) of the 5/6-fused acetoxy ketone **22a** [^{1}H NMR (360 MHz) δ 1.31 (s, 3 H), 1.76 (m, 1 H), 1.92 (s, 3 H), 2.54 (m, 4 H), 2.89 (d of d, J = 15, 4.0 Hz, 1 H), 4.30 (d, J = 6.1 Hz, 1 H), 5.97 (s, 1 H), 6.20 (d of d, J = 5, 12 Hz, 1 H), 7.53 (m, 3 H), 8.07 (m, 2 H); ^{13}C NMR (360 MHz) δ 13.98, 22.40, 27.25, 28.93, 36.29, 46.58, 72.83, 85.30, 128.80, 129.20, 129.68, 129.94, 165.46, 167.75, 170.61, 177.80, 208.31; IR ($CHCl_3$) 3010, 2980, 1745, 1720, 1700, 1630, 1610, 1590, 1585, 1455, 1390, 1375 cm^{-1}; high-resolution MS m/z calcd for $C_{17}H_{16}O_3$ (M - $C_2H_4O_2$ (HOAc)) 268.1100, obsd 268.1087]; and 0.28 g (18%) of the 5/6-fused hydroxy ketone **23** [^{1}H NMR (360 MHz) δ 1.16 (s, 3 H), 1.70 (m, 1 H), 2.31 (m, 1 H), 2.53 (m, 3 H), 2.79 (d of d, J = 4, 15 Hz, 1 H), 2.96 (m, 2 H), 5.26 (d of d, J = 5, 12 Hz, 1 H), 5.95 (s, 1 H), 7.47 (m, 2 H), 7.60 (m, 1 H), 8.06 (m, 2 H); ^{13}C NMR (360 MHz) δ, 14.69, 27.43, 36.15, 51.24, 60.30, 75.31, 78.38, 128.40, 128.94, 129.60, 129.71, 133.26, 166.31, 178.06, 209.00; IR ($CHCl_3$) 3500, 3400, 3030, 2990, 2900, 2880, 1730, 1710, 1690, 1585, 1500, 1450, 1390, 1385, 1375, 1280, 1100 cm^{-1}; high-resolution MS m/z calcd for $C_{17}H_{18}O_4$ (M$^+$) 286.1205, obsd 286.1209].

Irradiation of (1(*S*),7a(*S*))-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-5(7a*H*)-indanone (12g). Irradiation of 1.61 g (4.01 mmole) of **12g** for 1 h followed by workup in the manner as described gave 0.32 g (20%) of an inseparable mixture of tricyclic acetoxy ketones **27b** and **28b** in a 3.5:1 ratio as determined by NMR spectroscopy [^{1}H NMR (200 MHz) δ 1.01 (s, 3 H), 1.07 (s, 9 H), 1.23 (m, 2 H), 1.32–1.82 (br abs, 2 H), 2.06 (s, 0.63 H, OAc in **28b**), 2.12 (s, 2.69 H, OAc in **27b**), 2.18 (m, 1 H) 2.39 (d, J = 20 Hz, 0.21 H, C-4H in **28b**), 2.72 (d of d, J = 20, 6.5 Hz, 0.83 H, C-6H in **27b**), 2.86 (d, J = 20 Hz, 0.26 H, C-4H in **28b**) 4.20 (m, 1 H), 4.55 (s, 0.21 H, C-1H in **28b**), 4.67 (s, 0.76 H, C-1H in **27b**), 7.37 (m, 6 H), 7.68 (m, 4 H); IR ($CHCl_3$) 3010, 2930, 2870, 1745, 1730, 1615, 1360, 1200, 1100 cm^{-1}; high-resolution MS m/z calcd for $C_{24}H_{25}O_4Si$ (M - C_4H_9) (*tert*-butyl)) 405.1522, obsd 405.1539]; 0.30 g (19%) of the conjugated cyclopropyl ketone **31a** [^{1}H NMR (360 MHz) δ 1.03 (s, 3 H), 1.05 (s, 9 H), 1.10 (m, 1 H), 1.69 (m, 2 H), 1.86 (m, 2 H), 2.03 (s, 3 H), 2.39 (d, J = 5.6 Hz, 1 H), 2.78 (d, J = 17.65 Hz, 1 H), 3.00 (d, J = 17.7 Hz, 1 H), 4.08 (d of d, J = 7, 9.7 Hz, 1 H), 7.41 (m, 6 H), 7.69 (m, 4 H); ^{13}C NMR (360 MHz) δ 19.35, 21.85, 25.66, 26.90, 29.06, 31.73, 35.44, 41.59, 42.94, 55.89, 72.54, 80.11, 127.52, 127.59, 129.66, 129.68, 133.69, 134.00, 135.94, 170.00, 207.80; IR ($CHCl_3$) 3050, 2950, 2930, 2850, 1740, 1720, 1400, 1420, 1360, 1200, 1100, 900 cm^{-1}; high-resolution MS m/z calcd for $C_{22}H_{21}O_2Si$ (M - $C_6H_{13}O_2$ (*tert*-butyl + HOAc)), 345.1311, obsd 345.1306]; and 0.53 g (34%) of the 5/6-fused acetoxy ketone **22b** [^{1}H NMR (360 MHz) δ 1.03 (s, 9 H), 1.24 (s, 3 H), 1.54 (m, 1 H), 1.76 (m, 1 H), 1.83 (s, 3 H), 2.06 (m, 1 H), 2.28 (d of d, J = 6.8, 19.1 Hz, 1 H), 2.51 (m, 2 H), 3.91 (d, J = 6.3 Hz, 1 H), 4.87 (d of d, J = 11.4, 5 Hz, 1 H), 5.79 (s, 1 H), 7.38 (m, 6 H), 7.66 (m, 4 H); ^{13}C NMR (360 MHz) δ 13.10, 19.20, 11.50, 22.50, 26.75, 27.34, 30.78, 36.42, 45.95, 72.39, 87.66, 127.49, 128.4, 129.7, 133.30, 133.72, 135.77, 170.43, 178.82, 208.52; IR ($CHCl_3$) 3040, 3010, 2960, 2905, 2860, 1740, 1730, 1710, 1690, 1627, 1375, 1250, 1100 cm^{-1}; high-resolution MS m/z calcd for $C_{24}H_{25}O_4Si$ (M - C_4H_9 (*tert*-butyl)) 405.1522, obsd 405.1508].

Irradiation of 1-[[β-(Trimethylsilyl)ethoxy]methoxy]-7a-methyl-5(7a*H*)-indanone (12f). Irradiation of 3.09 g (10.5 mmole) of **12f** for 2.5 h followed by workup in the manner as described above gave 0.42 g (16%) of an inseparable mixture of tricyclic acetoxy ketone **27c** and **28c** in a ratio 3:1 ratio as determined by NMR spectroscopy [^{1}H NMR (360 MHz) δ 0.02 (s, 9 H), 0.95 (t, J = 8.5 Hz, 2 H), 1.01 (s, 2.64 H, CH_3 in **27c**), 1.03 (s, 0.87 H, CH_3 in **28c**), 1.39 (m, 1 H), 1.47 (d, J = 6.6 Hz, 1 H), 1.68 (m, 2 H), 2.09 (s, 0.89 H, OAc in **28c**), 2.10 (s, 2.79 H, OAc in **27c**), 2.22 (d, J = 20 Hz, 1 H, C-6H in **27c**), 2.74 (d, J = 20 Hz, 0.28 H, C-4H in **28c**), 2.78 (d of d, J = 20, 6.7 Hz, 0.86 H, C-6H in **27c**), 2.85 (d, J = 20 Hz, 0.22 H, C-4H in **28c**), 4.03 (d, J = 4.7 Hz, 0.78 H, C-1H in **27c**), 4.06 (d, J = 4.8 Hz, 0.21 H, C-1H in **28c**), 4.60 (s, 0.66 H, C-4H in **27c**), 4.64 (s, 0.33 H, C-6H in **28c**), 4.73 (m, 2 H); IR ($CHCl_3$) 3020, 2960, 2900, 1745, 1410, 1375, 1210, 1020, 830, 690 cm^{-1}; high-resolution MS calcd for $C_{16}H_{27}O_3Si$ (M - $C_2H_3O_2$ (OAc)) 295.1730 obsd 295.1692]; 0.40 g (16%) of the hemiacetal acetate **34** [^{1}H NMR (360 MHz) δ 0.012 (s, 9 H), 0.94 (t, J = 8.5 Hz, 2 H), 1.95 (m, 1 H), 2.05 (s, 3 H), 2.20 (s, 3 H), 2.65 (m, 1 H), 3.73 (m, 4 H), 4.81 (d of d, J = 6.8, 33 Hz, 2 H), 6.05 (t, J = 5.3 Hz, 1 H), 6.61 (m, 2 H), 6.99 (d, J = 8 Hz, 1 H); IR ($CHCl_3$) 3200, 3940, 2870, 1725, 1610, 1420, 1210, 1020 cm^{-1}; high-resolution MS m/z calcd for $C_{16}H_{27}O_3Si$ (M - $C_2H_3O_2$ (OAc) 295.1730; obsd 295.1694]; 0.27 g (11%) of the conjugated cyclopropyl ketone **31b** [^{1}H NMR (200 MHz) δ 0.01 (s, 9 H), 0.88 (t, J = 8.5 Hz, 2 H), 1.21 (s, 1 H), 1.27 (s, 2 H), 1.89 (d, J = 5.4 Hz, 1 H), 2.15 (m, 5 H), 2.45 (d, J = 17.7 Hz, 1 H), 2.99 (d, J = 17.6 Hz, 1 H), 3.63 (m, 2 H), 4.05 (d of d, J = 6.8, 9.1 Hz, 1 H), 4.72 (m, 2 H); IR ($CHCl_3$) 3020, 2960, 2900, 1720, 1420, 1375, 1210, 1020, cm^{-1}; high-resolution MS m/z calcd for $C_{15}H_{21}O_5$ (M - C_3H_9Si (TMS) 281.1389, obsd 281.1299]; 0.47 g (18%) of the aldehyde **13**; 0.11 g (5%) of a compound with spectral data expected for the 5/6-fused linear dienone **33b** [^{1}H NMR (200 MHz) δ 0.05 (s, 9 H), 0.95 (t, J = 8.5 Hz, 2 H), 1.93 (s, 3 H), 2.03 (m, 2 H), 2.75 (m, 4 H), 3.70 (m, 2 H), 4.19 (t, J = 4.5 Hz, 1 H), 4.80 (m, 2 H), 5.96 (s, 1 H)]; and 0.82.g (32%) of the 5/6-fused acetoxy ketone **22c** [^{1}H NMR (360 MHz) δ 0.03 (s, 9 H), 0.97 (m, 2 H), 1.12 (s, 3 H), 1.55 (m, 1 H), 2.04 (s, 3 H), 2.24 (m, 1 H), 2.42 (m, 3 H), 2.80 (d of d, J = 1.3, 5.1 Hz, 1 H), 3.64 (m, 2 H), 4.09 (d, J = 6.3 Hz, 1 H), 4.74 (m, 2 H), 4.83 (d of d, J = 4.9, 11.6 Hz, 1 H), 5.9 (s, 1 H); ^{13}C NMR (360 MHz) δ -1.45, 13.46, 18.04, 22.6, 27.53, 28.37, 36.24, 46.33, 65.37, 76.65, 86.81, 94.66, 128.73, 170.80, 178.70, 208.45; IR ($CHCl_3$) 3015, 2970, 2900, 1740, 1720, 1635, 1375, 1250, 1040 cm^{-1}; high-resolution MS m/z calcd for $C_{16}H_{27}O_3Si$ (M - $C_2H_3O_2$ (OAc)) 295.1730, obsd 295.1683].

Acknowledgment. We wish to thank Dr. Ken Belmore and Mr. Adam Kois for their assistance in acquiring and interpreting NMR spectral data and Mr. Ley Hathcock and Dr. Russell Timkovich for mass spectral analyses. Grants from the National Institutes of Health and the National Science Foundation for the purchase of high-resolution NMR instrumentation and from the National Institutes of Health for the purchase of a high-resolution mass spectrometer are gratefully acknowledged. One of us (P.L.K.) wishes to thank the University of Alabama for a Graduate Council Research Fellowship.

Registry No. 7, 104012-37-5; **11a**, 16271-49-1; **11b**, 41878-38-0; **11c**, 41878-37-9; **11c** (6-phenylseleno derivative), 135878-27-2; **11d**, 135878-18-1; **11e**, 135878-22-7; **11f**, 135969-56-1; **11f** (6-phenylseleno derivative), 135878-28-3; **11g**, 102650-61-3; **11g** (6-phenylseleno derivative), 135878-29-4; **11h**, 126541-54-6; **11h** (6-phenylseleno derivative), 135878-30-7; **12a**, 135878-01-2; **12b**,

135878-12-5; **12c**, 135878-15-8; **12d**, 135878-19-2; **12e**, 135878-23-8; **12f**, 135878-25-0; **12g**, 135878-26-1; **13**, 135878-02-3; **18**, 135878-03-4; 18 (phenylseleno derivative), 135878-31-8; **19**, 97400-51-6; **20a**, 61950-54-7; **21a**, 135878-04-5; **22a**, 135878-05-6; **22b**, 135912-60-6; **22c**, 135878-24-9; **23**, 135878-06-7; **27a**, 135878-07-8; **27b**, 135878-13-6; **27c**, 135878-20-5; **28a**, 135878-08-9; **28b**, 135878-14-7; **28c**, 135878-21-6; **31a**, 135878-09-0; **31b**, 135878-16-9; **33a**, 135878-10-3; **33b**, 135878-17-0; **34**, 135878-11-4.

Supplementary Material Available: ^1H and in some cases ^{13}C NMR spectra for all relevant compounds (32 pages). Ordering information is given on any current masthead page.

Phototransposition Chemistry of 1-Methylpyrazole. Deuterium, Methyl, and Fluorine Substitution

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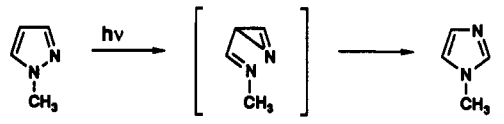
Received April 29, 1991

1-Methylpyrazole (1) was observed to undergo photo-ring cleavage to 3-(*N*-methylamino)propenenitrile (17) and phototransposition to 1-methylimidazole (3). Although upon prolonged irradiation 17 is also converted to 3, the efficiency of the 1 → 17 → 3 pathway is low and cannot account for a significant fraction of 3 observed upon short-duration irradiation. Under these conditions, deuterium-labeling studies show that 1 phototransposes to 3 by the P_4, P_6, and P_7 permutation patterns in a ratio of 4.8:6.5:1.0. These scrambling patterns are consistent with mechanisms involving ring contration–ring expansion (P_4) and electrocyclic ring closure followed by one (P_6) or two (P_7) sigmatropic shifts of nitrogen. Methyl and fluorine substitution on the 1-methylpyrazole ring reduces reactivity via the P_6 and P_7 pathways. Thus, 1,5-dimethylpyrazole transposes by these pathways in a ratio of 3.5:1.8:1.0, whereas 5-fluoro-1-methylpyrazole isomerizes only by the P_4 and P_6 pathways in a ratio of 9.7:1.

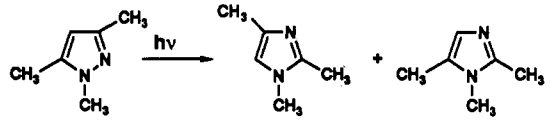
Introduction

The phototransposition chemistry of N-substituted pyrazoles has been of interest[1] since Schmid and co-workers[2] originally reported that 1-methylpyrazole (1) undergoes photoisomerization to *N*-methylimidazole (3). Although



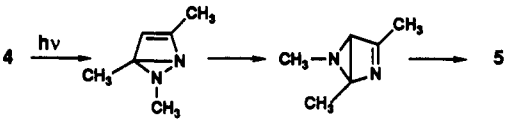
1 2 3

the transposition was rationalized in terms of a ring contraction–ring expansion mechanism,[2] involving the intermediacy of 2-(*N*-methylimino)-2*H*-azirine (2), subsequent studies implicated the operation of other transposition pathways. Thus, Beak and co-workers observed that 1,3,5-trimethylpyrazole (4) phototransposes to 1,2,4-trimethylimidazole (5) and 1,2,5-trimethylimidazole (6).[3]

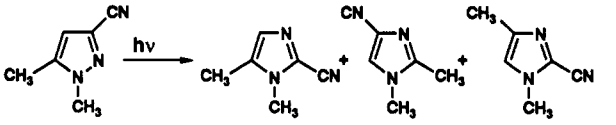


4 5 6

Although 6 results from the 2,3-interchange demanded by the ring contraction–ring expansion mechanism, product 5 cannot be rationalized by this mechanistic pathway. Rather, this product was suggested to arise via a transposition pathway that included initial electrocyclic ring closure, [1,3]-sigmatropic shift of nitrogen, and rearomatization of the resulting 2,5-diazabicyclo[2.1.0]pentene to provide 5.[3]

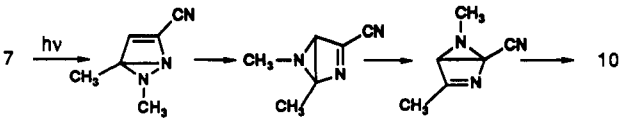


Barltrop, Day, and colleagues later observed that 3-cyano-1,5-dimethylpyrazole (7) undergoes phototransposition to three primary products, 8 and 9, which can be



7 8 9 10

rationalized by the ring contraction–ring expansion mechanism and the one-step nitrogen walk mechanism, respectively, and 10, which cannot arise by either of these transposition pathways but was suggested to arise via a double nitrogen walk mechanism.[4] Such a double walk



had formerly been implicated in the phototransposition chemistry of cyanothiophenes[5] and cyanopyrroles.[6,7] In-

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0022-3263/91/1956-6313$02.50/0