4-Methyl-1-oxaspiro[4.5]decane (66). Mixture of diastereoisomers: yield 0.13 g (85%); oven temperature 110–115 °C (10 Torr); IR (film) 1149, 1074, 1040 cm^{-1}; 80-MHz ^1H NMR ($CDCl_3$) δ 0.97 (3 H, d, J = 6.94 Hz), 1.11–2.32 (13 H, complex absorption), 3.80 (2 H, m). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.82; H, 12.09.

4,8-Dimethyl-1-oxaspiro[4.5]decane (67).[10] Mixture of diastereoisomers: yield 0.10 g (92%); oven temperature 95 °C (15 Torr) (lit.[10] 91 °C (15 Torr)).

Acknowledgment. Financial support from the Dirección General de Investigación Científica y Técnica (Project PB88-0241) and LUCTA S.A. is gratefully acknowledged.

Intramolecular Addition Reactions of Carbonyl Ylides Formed during Photocyclization of Aryl Vinyl Ethers

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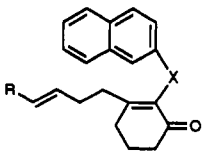
Received May 3, 1991

Photocyclization of aryl vinyl ethers reportedly proceeds via carbonyl ylide intermediates. The photochemical behavior of several aryl vinyl ethers, which incorporate a pendant alkene side chain, was explored. Naphthyl vinyl ethers **1c** and **1d** provided products that are consistent with photocyclization and subsequent intramolecular ylide–alkene addition. Product distribution is influenced by solvent and temperature effects. Thus, irradiation of **1c** in toluene provides **9a** in 87% yield. However, irradiation of **1c** in methanol/toluene (1:1) provides **3c** (45%), **11** (24%), and **12** (23%). Product **12** results from photoinitiated intramolecular [2 + 2] cycloaddition of the butenoate ester side chain to the naphthalene system.

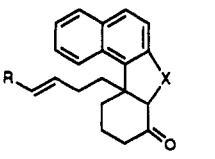
Introduction

Photocyclization of aryl vinyl ethers reportedly proceeds via a six-electron rearrangement to provide carbonyl ylide intermediates. In the absence of other effects these systems rearrange by a process involving hydrogen shifts to provide dihydrofuran products.[1,2] Although the literature is abundant with examples of carbonyl ylide cycloadditions, surprisingly little use has been made of the aryl vinyl ether photolysis for preparation of these 1,3-dipoles.[3] Usual methods for the generation of the carbonyl ylide species have involved thermolysis and photolysis of oxirane rings,[4] carbene addition to carbonyl groups,[5] and extrusion reactions such as the thermolysis of oxadiazolines.[6] We report here some preliminary results on the intramolecular addition reactions of carbonyl ylides, which are generated on photolysis of aryl vinyl ethers.

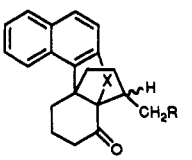
Recently, we reported that aryl vinyl sulfides bearing a pendant alkene side chain undergo photocyclization and subsequent intramolecular ylide–alkene addition.[7-9] Significant structure and temperature effects have been noted for the photocyclization–intramolecular addition of aryl vinyl sulfides. It is of interest therefore to compare the products of these reactions with those from the aryl vinyl ether photolyses described below. In summary, photolysis of **1a** with Pyrex-filtered light favors formation of hydrogen shift product **2a** at low temperatures (–78 °C to room temperature) and intramolecular addition product **3a** at high temperature (110 °C). Conversely, photolysis of **1b** provides **3b** as the major product regardless of the temperature employed (–78 to 110 °C).[10]



1a, X = S, R = H
b, X = S, R = CO_2Et
c, X = O, R = CO_2Et
d, X = O, R = H



2a, X = S, R = H
b, X = O, R = CO_2Et
c, X = O, R = H



3a, X = S, R = H
b, X = S, R = CO_2Et
c, X = O, R = CO_2Et
d, X = O, R = H

Results and Discussion

Aryl vinyl ether **1c** was prepared from 3-ethoxycyclohexenone via the epoxide **6a** as shown. Photolysis of a

(1) For reviews see: Schultz, A. G. *Acc. Chem. Res.* **1983**, *16*, 210. Schultz, A. G.; Motyka, L. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 1.

(2) Wolff, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6157. Wolff, T. *J. Org. Chem.* **1981**, *46*, 978.

(3) (a) For a recent review of 1,3-dipolar cycloaddition chemistry, see: *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley Interscience: New York, 1984; Vol. 1–2. (b) For a review of intramolecular dipolar cycloaddition reactions, see: Padwa, A. In *New Synthetic Methods*; Verlag Chemie: New York, 1979; Vol. 5, pp 25–69. (c) *Advances in Cycloaddition*; Curran, D. P., Ed.; Jai Press: Greenwich, CT, 1988; Vol. 1.

(4) Eberbach, W.; Brokatzky, J.; Fritz, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 47. Eberbach, W.; Brokatzky, J. *Tetrahedron Lett.* **1980**, 4909. Trossolo, A. M.; Leslie; T. M.; Sarpotdar, A. S., Small, R. D.; Ferraudi, G. J. *Pure Appl. Chem.* **1979**, *51*, 261. Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 153 and 159.

(5) Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100. Padwa, A.; Hornbuckle, S. F.; Fryxell, G. E.; Stull, P. D. *J. Org. Chem.* **1989**, *54*, 817.

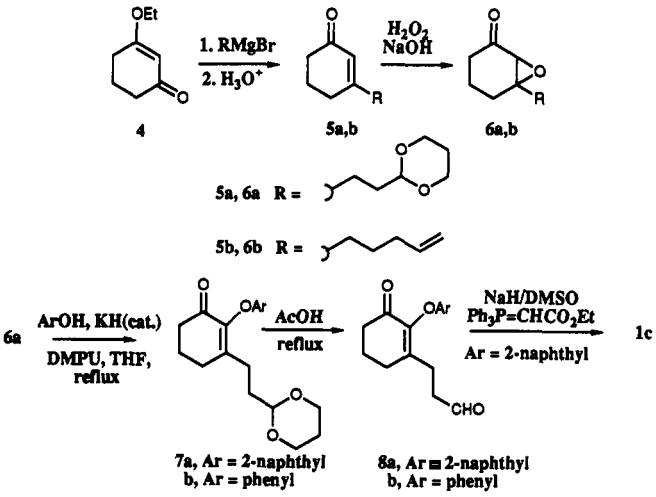
(6) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 4260.

(7) Dittami, J. P.; Ramanathan, H.; Breining, S. *Tetrahedron Lett.* **1989**, *30*, 795.

(8) Dittami, J. P.; Nie, X.-Y. *Synth. Commun.* **1990**, *20*(4), 541.

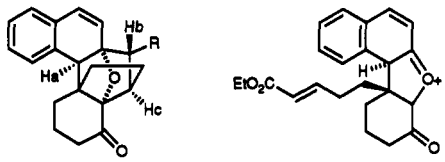
(9) Dittami, J. P.; Nie, X.-Y.; Buntel, C.; Rigatti, S. *Tetrahedron Lett.* **1990**, 3821.

0022-3263/91/1956-5572$02.50/0



solution of **1c** in toluene afforded **9a** as the major product at all temperatures examined (−78 to 110 °C).[10] In a typical experiment, a solution of **1c** in toluene (10^{-3} M) was irradiated for 25 min through Pyrex to give **9a** in 85% yield after chromatography on silica gel. In some cases trace amounts of the addition product **3c** were observed in the reaction mixtures. However, none of the hydrogen shift product **2b** was detected in any of these experiments.

Formation of **9a** is consistent with a photoinduced six-electron conrotatory cyclization to give a trans-fused ylide intermediate **10** that undergoes subsequent intramolecular [3 + 2] dipolar cycloaddition to the side-chain olefin.[1] The



9a, R = CO_2Et
b, R = H

10

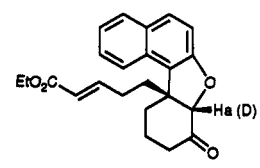
mechanism for formation of **3c** is less obvious but may involve either an intramolecular Michael addition (vide infra) or an intramolecular enelike reaction occurring from the intermediate carbonyl ylide **10**.[9,11] Control experiments were carried out with the [3 + 2] cycloadduct **9a**, which demonstrate that it is not an intermediate in the formation of **3c**. Thus, pure **9a** remains unchanged upon resubjection to the photolysis conditions. Furthermore, **9a** is thermally stable at temperatures well above those used for the photolysis. Thus, **9a** remains unchanged when heated in a solution of toluene for 30 min at reflux temperature. The product composition from the aryl vinyl ether photolysis differs significantly from reactions involving aryl vinyl sulfide **1b**. This difference may reflect a higher reactivity (or lower stability) for the intermediate carbonyl ylide systems.

The structural assignment for **9a** was made on the basis of IR, MS, and 200- and 600-MHz ^1H and ^{13}C NMR data. Confirmation of structure was obtained by single-crystal X-ray analysis. The 200-MHz spectrum of **9a** displays cleanly resolved signals for Ha (s, δ 3.51), Hb (d, J = 3.88 Hz, δ 2.58), and Hc (m, δ 3.00). The unusually low chemical shifts for Ha and Hc are attributed to deshielding by the syn oxygen of the oxabicyclo [2.2.1] ring system.[12] The relatively small observed coupling between Hb and Hc (3.88 Hz, dihedral angle ~121°) is consistent with the stereochemical assignment. The styrene protons are also cleanly resolved in the NMR spectrum appearing as doublets at δ 6.35 and 6.50 (J = 9.9 Hz). COSY, NOSEY, and heteronuclear shift-correlated 2-D NMR spectra have also been obtained for this system.

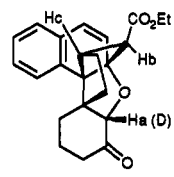
The high-yield preparation of **9a** is significant. In a single experimental operation three new rings and six chiral centers are formed with excellent stereocontrol. Thus, the photoinitiated aryl vinyl ether route to carbonyl ylide systems shows good potential for use in synthesis.

We have noted some interesting wavelength and solvent effects on the photolysis reactions of **1c**. In general, cleaner product mixtures were obtained when a lower energy light source was employed for the photolysis. Thus, irradiation of **1c** (10^{-3} M in toluene) with a 366-nm light source provides the [3 + 2] adduct **9a** in 87% yield after chromatography on silica gel.[13] Moreover, none of the adduct **3c** was observed in any of these product mixtures.

If the photolysis of **1c** is carried out in a solution of toluene/methanol (1:1; 10^{-3} M) at 366 nm, none of the usual [3 + 2] adduct **9a** is obtained. Rather, we observe formation of **3c** (45%), **11** (24%), and **12** (23%) (isolated



11



12

yields after chromatography). Formation of **11** can occur by protonation of the intermediate carbonyl ylide **10**. Presumably, the stereochemical relationship of Ha and the side chain in product **11** is cis as shown. In related systems NMR signals corresponding to Ha appear at δ 4.4–4.6 for the cis-fused dihydrofurans and at δ 5.0–5.2 for the trans-fused species. The signal for Ha in compound **11** appears at δ 4.7. In conclusion, ylide protonation effectively competes with the intramolecular [3 + 2] cycloaddition and proceeds to give the more stable cis isomer. The latter finding is consistent with earlier work.[1]

The enhanced yield of adduct **3c** in toluene/methanol is consistent with intramolecular Michael addition to the side chain and subsequent protonation of the ester enolate by the solvent methanol. To test this hypothesis the photolysis of **1c** was carried out in a mixture of toluene/methanol-*d* (1:1). Interestingly, a significant deuterium isotope effect was noted. Thus, the major product isolated from the reaction carried out in methanol-*d* was the intramolecular adduct **3c** with only trace amounts of the products **11** and **12** (<15% of both). As expected, the product **3c** showed incorporation of a single deuterium by analysis on the mass spectrum. The site of deuterium incorporation at the center adjacent to the ester group was confirmed by ^2H NMR, which displayed a resonance at δ 2.3.[14] Products **11** and **12** from this reaction were also

(10) Photochemical experiments were conducted using a 450-W Canrad-Hanovia medium-pressure quartz mercury-vapor lamp. The lamp was placed in a water-cooled Pyrex immersion well. Reaction solutions were saturated with argon prior to irradiation. For high- and low-temperature runs a vacuum-jacketed quartz immersion well was employed with a Pyrex sleeve filter. The immersion well was placed in a large-scale (~200 mL) reactor. Heating was carried out with a silicon oil bath, and cooling was achieved with a Neslab ULT-80DD low-temperature circulating bath.

(11) A similar mechanism was proposed for the formation of **3b**. See ref 9.

(12) Ouellette, R. J.; Roenblum, A.; Booth, G. *J. Org. Chem.* **1968**, *33*(11), 4302. Lee, M. W.; Herndon, W. C. *J. Org. Chem.* **1978**, *43*(3), 518. For a similar example involving the thiabicyclo[2.2.1]heptane series, see: Cava, M. P.; Pollack, N. M. *J. Am. Chem. Soc.* **1967**, *89*(14), 3639.

(13) The Pyrex hanovia light source was fitted with a 366-nm filter prepared from Corning glass filters CS 0-52 and CS 7-37.

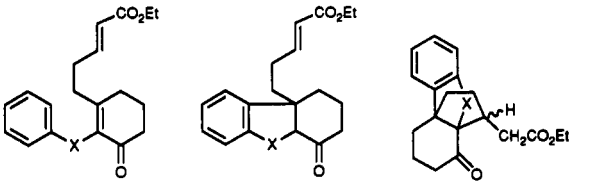
examined. Indeed, both showed deuterium incorporation by mass spectral analysis. Furthermore, the absence of signals at δ 4.67 and 4.14 in the ^1H NMR spectrum of **11** and **12**, respectively, as well as the appearance of signals at δ 4.67 and 4.14 in the ^2H NMR spectrum of each is consistent with deuteration at Ha. Finally, we have demonstrated an intramolecular Michael reaction that occurs by a dark process. Thus, treatment of **11** with Na_2CO_3 in benzene/methanol (1:1) at room temperature for 2 h provided **3c** in 89% yield.

Compound **12** presumably results from ylide protonation to give the cis-fused dihydrofuran **11** followed by intramolecular [2 + 2] cycloaddition.[15] Support for the intermediacy of **11** in the formation of **12** is given by the following experiment. A sample of **11** was isolated and resubjected to the conditions of the photolysis (366-nm light source, room temperature), and the progress of the reaction was followed by ^1H NMR. After 4.5-h reaction time we observed 76% conversion to **12**. At higher energy wavelengths (Pyrex-filtered light) the conversion to **12** is even more rapid (~75% conversion after 40 min). However, under these conditions **12** undergoes further rearrangement to a product for which a structure has not yet been determined.

The NMR spectrum of **12** is very similar to that of **9a** with resonances for Ha (s, δ 4.17), Hb (d, J = 4.76 Hz, δ 3.02), and Hc (m, δ 3.06). In benzene-d_6 the signals for Hb and Hc resolve as Hb (d, J = 4.77 Hz, δ 2.95) and Hc (m, δ 3.13). Verification of structure **12** was obtained by single-crystal X-ray analysis.

Earlier, we reported that the photocyclization of **1d** gave both **2c** and **3d** at room temperature.[7] Upon reexamination of this reaction at elevated temperature (110 °C) we observed a mixture of products that contained **9b** and **3d** (~4:1 ratio **9b**:**3d** by ^1H NMR analysis). The structure of compound **9b** was confirmed by X-ray analysis. Interestingly, the crystal that was examined consisted of a single enantiomer. Unfortunately, the absolute configuration could not be determined since no suitable heavy atom was present in the molecule.

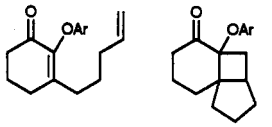
The photolysis reactions of the phenyl-substituted system **13a** were also examined. Compound **13a** was prepared from **6a** in a manner analogous to the preparation of **1c**. Photolysis of **13a** in toluene (10^{-3} M) at temperatures ranging from 25 to 110 °C provided only ring-closed product **14a**. None of the intramolecular addition product **15a** was observed in the photolysis mixtures. These results contrast those for the corresponding sulfur analogue **13b** where formation of **15b** is observed albeit to a limited extent.[9] Both **14a** and **14b** remain unchanged upon resubjection to the photolysis conditions used in their formation. However, treatment of either **14a** or **14b** with sodium carbonate in methanol/benzene (1:1; *in the dark*) provides the intramolecular Michael addition product **15a** or **15b** in 57 and 54% yield, respectively.



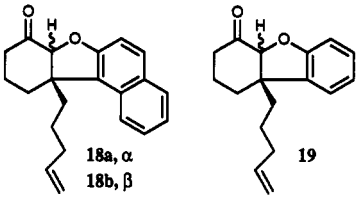
13a, X = O; **b**, X = S — **14a**, X = O; **b**, X = S — **15a**, X = O; **b**, X = S

The photochemistry of systems such as **16** that incorporate a five-carbon alkene side chain was also examined. These compounds are readily prepared from **6b** by the same procedures used for the preparation of **7a** and **7b**.

Surprisingly, photolysis of **16a** did not provide any intramolecular addition product. Rather, we observed formation of **17a** and **18** as the major products.[16] (Product **18** was obtained as a mixture of isomers at Ha.) Compound **17a** is consistent with intramolecular [2 + 2] cycloaddition to the enone system.[17] Formation of **18** presumably involves a six-electron photocyclization followed by either an inter- or intramolecular hydrogen transfer. The phenyl-substituted system **16b** provided similar results as shown.



16a, Ar = 2-naphthyl; **b**, Ar = phenyl — **17a**, Ar = 2-naphthyl; **b**, Ar = phenyl



18a, α; **18b**, β — **19**

In summary, we have demonstrated that the photoinitiated aryl vinyl ether approach to carbonyl ylides shows good potential for use in organic synthesis. The tandem photocyclization–intramolecular addition of aryl vinyl ethers provides a facile route to complex multicyclic systems from simple achiral starting materials. Future investigations will explore applications of this method to the synthesis of biologically active compounds.

Experimental Section

General Methods. High-resolution ^1H NMR spectra were obtained by Dr. Charles Rodger of Spectrospin AG on a Bruker AMX 600 (600 MHz) using an inverse detection probehead. Low-resolution spectra were recorded on a Bruker ACE 200 (200 MHz) NMR spectrometer. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane at 0.00. Carbon nuclear magnetic resonance spectra were recorded at 50.3 MHz. Deuterium NMR spectra were recorded at 30.72 MHz in CH_2Cl_2 as solvent, and deuterium chemical shifts are reported in ppm (δ) relative to $CDCl_3$ (7.24) internal standard. Electron-impact mass spectra

(14) Analyses of products from the deuterium-labeling studies were carried out on a Hewlett-Packard GC–MS system as described in the Experimental Section. All products were compared with products obtained in control experiments (methanol-*d* vs methanol-*h*). Deuterium NMR was measured on a Bruker ACE-200 spectrometer at 30.72 MHz in CH_2Cl_2 as solvent. Chemical shifts are reported in ppm (δ) relative to $CDCl_3$ (7.24) internal standard.

(15) For a recent report on the photochemical [2 + 2] cycloadditions of butenoxyacetonaphthones, see: Wagner, P. J.; Sakamoto, M. *J. Am. Chem. Soc.* **1989**, *111*, 9254. For a report on the intramolecular [2 + 2] cycloaddition of naphthonitrile systems, see: McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L.; Faggiani, R. *J. Am. Chem. Soc.* **1982**, *104*, 4644. For a report on the inter- and intramolecular [2 + 2] photocycloadditions of enol ethers to naphthalene, see: Gilbert, A.; Heath, P.; Kashoulis-Koupparis, A.; Ellis-Davies, G. C. R.; Firth, S. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 31. For studies on the [2 + 2] photocycloaddition of acrylonitrile to naphthalene, see: Bowman, R. M.; Chamberlain, T. R.; Huang, C. W.; McCullough, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 692. Bowman, R. M.; Calvo, C.; McCullough, J. J.; Miller, R. C.; Singh, I. *Can. J. Chem.* **1973**, *51*, 1060. Bowman, R. M.; McCullough, J. J. *Chem. Commun.* **1970**, 948.

(16) Structural assignment is based on ^1H NMR, IR, MS.

(17) For similar intramolecular [2 + 2] photocycloadditions of cyclohexenones, see: Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135. Pirrung, M. C. *J. Am. Chem. Soc.* **1981**, *103*, 82. Hoye, T. R.; Martin, S. J.; Peck, D. R. *J. Org. Chem.* **1982**, *47*, 331. Fetizon, M.; Lazare, S.; Pascard, C.; Prange, T. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1407.

were obtained on a Hewlett-Packard GC–MS system consisting of a Hewlett-Packard 5890A gas chromatograph, a 25 m × 0.32 mm capillary column (Perkin-Elmer p.n. 009-23-27) packed with bonded methyl 5% phenyl silicone (25-μm film thickness), and a Hewlett-Packard 5970B mass selective detector with 70-eV electron energy. Infrared spectra (IR) were recorded on a Perkin-Elmer 683 infrared spectrometer or a Perkin-Elmer 1720 FT-IR infrared spectrometer. Ultraviolet spectra (UV) were recorded on a Shimadzu UV 21000U UV–vis recording spectrophotometer or a Perkin-Elmer 553 UV–vis spectrophotometer. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Elemental analysis was performed by either Galbraith Laboratories, Knoxville, TN, or Quantitative Technologies, Inc., Bound Brook, NJ. High-resolution mass spectrometry was carried out on a Kratos Concept-1S double-focusing instrument. Samples were introduced from a heated direct insertion probe and ionized by electron ionization.[18] Single-crystal X-ray analysis was determined on a Nicolet R3m/μ diffractometer. A representative crystal was surveyed, and a 1-Å data set (maximum sin θ/λ = 0.5) was collected. Precise information on the crystallographic calculations, coordinates, anisotropic temperature factors, distances, and angles are available as supplementary material.[19] Diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium/benzophenone just prior to use. Toluene, benzene, and methylene chloride were distilled under nitrogen from calcium hydride immediately prior to use. Flash chromatography was performed on J. T. Baker 40-μm silica gel under a positive pressure of nitrogen. Triethylamine-deactivated silica gel columns were prepared by washing the silica gel with a mixture of hexane and triethylamine (10:1). The column was then rinsed with three column volumes of hexane and one column volume of elution solvent to purge excess triethylamine.

3-[2-(1,3-Dioxan-2-yl)ethyl]-2-cyclohexen-1-one (5a). To a 100-mL flask equipped with a reflux condenser was added magnesium turnings (1.94 g, 80 mmol) and THF (50 mL) followed by the slow addition of 2-(2-bromoethyl)-1,3-dioxane (11.7 g, 60 mmol). The exothermic reaction was maintained at reflux temperature for 10 min and then cooled to 0 °C. A solution of 3-ethoxy-2-cyclohexen-1-one (8.42 g, 60 mmol) in THF (40 mL) was added over 40 min, and the resulting mixture was stirred at room temperature for 2 h. Solvent was removed at reduced pressure, and the residue was partitioned between methylene chloride and a saturated aqueous solution of oxalic acid. The aqueous phase was further washed with methylene chloride, and the combined organic phases were washed with water and brine and dried (Na_2SO_4). Solvent was removed on a rotary evaporator, and the residue was distilled to yield **5a** as a light yellow oil (8.69 g, 82%): bp 150 °C (1.2 mm Hg); IR (film) 2950, 2860, 1660, 1620 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.26–1.32 (d, 1 H, J = 13.67 Hz), 1.67–2.32 (m, 10 H), 3.62–3.76 (dt, 2 H, J = 12.29 and 2.30 Hz), 3.99–4.07 (dd, 2 H, J = 10.77 and 5.03 Hz), 4.48 (t, 2 H, J = 4.95 Hz), 5.81 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.49, 25.52, 25.65, 29.51, 31.88, 32.04, 37.13, 66.66, 100.90, 125.38, 165.60, 199.53; GC/MS (EI, 70 eV) m/e 210 (M^+), 110, 101, 100. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.28; H, 8.80.

3-(4-Pentenyl)-2-cyclohexenone (5b). To a mixture of Mg turnings (1.5 g, 62 mmol) in dry THF (40 mL) was added 5-bromo-1-pentene (5.5 mL, 43 mmol). The solution was maintained at reflux temperature during the addition. After 15 min, a solution of 3-ethoxy-2-cyclohexenone (5 g, 36 mmol) in THF (35 mL) was added. The mixture was stirred for 45 min, after which aqueous saturated NH_4Cl solution (100 mL) was added. The yellow suspension was extracted with dichloromethane, and the organic phase was washed with water and brine and dried (Na_2SO_4). Solvent was removed under reduced pressure to afford a yellow oil that was stirred for 1 h in a solution of HCl (1 N, 10 mL) and ethanol (25 mL). The solution was neutralized with solid sodium bicarbonate. Ethanol was removed under reduced pressure, and the crude product was partitioned between water and ether. The aqueous phase was extracted with dichloromethane, and the combined organic phases were washed with water and brine and dried (Na_2SO_4). Distillation gave **5b** (4.25 g, 72%): bp 105–110 °C (1.5 mm Hg); IR (film) 3080, 2940, 1670, 1640, 1625 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.5–2.4 (m, 12 H), 4.9–5.1 (m, 2 H), 5.7–5.9 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.60, 25.92, 29.56, 33.04, 37.22, 115.13, 125.64, 137.72, 166.13, 199.72; GC/MS (EI, 70 eV) m/e 164 (M^+), 136, 123, 108, 93. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.26; H, 9.68.

6-[2-(1,3-Dioxan-2-yl)ethyl]-7-oxabicyclo[4.1.0]heptan-2-one (6a). A mixture of **5a** (3.15 g, 15 mmol), hydrogen peroxide (30%, 4.42 mL, 39 mmol), and methanol (50 mL) was maintained at 10–15 °C while a solution of sodium hydroxide (0.66 g, 16.5 mmol) in water (30 mL) was added over 1 h. Following the addition, stirring was continued for an additional 30 min at 10 °C after which the aqueous solution was extracted with methylene chloride. The combined organic phases were washed with brine and dried (Na_2SO_4). Solvent was removed under reduced pressure to afford a crude oil (2.40 g), which was purified by chromatography on silica gel deactivated with triethylamine (hexane/ethyl acetate (5:1)) to provide **6a** (2.07 g, 63%): IR (film) 2960, 2850, 1710 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.34 (m, 1 H), 1.7–2.1 (m, 10 H), 2.45–2.56 (m, 1 H), 3.09 (s, 1 H), 3.67–3.80 (t, 2 H, J = 12.34 Hz), 4.03–4.11 (dd, 2 H, J = 10.79 and 5.09 Hz), 4.51–4.56 (t, 1 H, J = 4.29 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 17.27, 25.51, 26.1, 29.93, 30.14, 35.76, 61.25, 64.86, 66.73, 101.18, 208.70; GC/MS (EI, 70 eV) m/e 226 (M^+), 196, 150, 122, 113. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.64; H, 8.38.

6-(4-Pentenyl)-7-oxabicyclo[4.1.0]heptan-2-one (6b). According to the procedure described for preparation of **6a**, a solution of alkene **5b** (2.7 g, 16.4 mmol) in methanol (15 mL) was treated with hydrogen peroxide (5 mL, 30%) and a solution of sodium hydroxide (6 N, 1.3 mL) to give **6b** as a colorless oil (2.5 g, 86%) that was used in the subsequent step without purification: IR (film) 3080, 2940, 2860, 1710, 1645 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.5–2.2 (m, 11 H), 2.4–2.6 (m, 1 H), 3.1 (s, 1 H), 4.9–5.1 (m, 2 H), 5.7–5.9 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 17.17, 23.66, 26.25, 33.24, 35.16, 35.79, 60.93, 65.10, 115.04, 137.73, 206.73. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.29; H, 8.95. Found: C, 73.41; H, 9.09.

3-[2-(1,3-Dioxan-2-yl)ethyl]-2-(2-naphthalenyloxy)-2-cyclohexen-1-one (7a). A solution of epoxide **6a** (2.26 g, 10 mmol) in THF (20 mL) was added to a solution of KH (40% in mineral oil, 0.11 g) and 2-naphthol (1.73 g, 12 mmol) in THF (25 mL). *N,N'*-Dimethylpropyleneurea, DMPU (1.7 mL), was added, and the mixture was stirred at reflux temperature for 40 h. The solvent was removed under reduced pressure, and the residue was partitioned between methylene chloride and water. The aqueous phase was further extracted with methylene chloride, and the combined extracts were washed with water and brine and dried (Na_2SO_4). Removal of solvent at reduced pressure and chromatography of the residue on silica gel (hexane/ethyl acetate (3:1)) gave **7a** (1.71 g, 48.5%). The product could be further purified by crystallization from ethyl acetate/hexane to give **7a** as a light yellow solid: mp 105.5–106.6 °C; IR (film) 3060, 2960, 2860, 1680, 1630, 1600, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.22 (m, 2 H), 1.72–2.15 (m, 6 H), 2.3–2.6 (m, 5 H), 3.65 (dt, 2 H, J = 12.27 and 2.62 Hz), 4.05 (dd, 2 H, J = 10.71 and 5.06 Hz), 4.45 (t, 1 H, J = 5.05 Hz), 7.0 (d, 1 H, J = 2.41 Hz), 7.23 (dd, 1 H, J = 2.51 and 8.91 Hz), 7.30–7.42 (m, 2 H), 7.65 (d, 1 H, J = 7.58 Hz), 7.77 (d, 2 H, J = 8.71 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.15, 25.48, 25.99, 29.40, 32.20, 38.31, 66.61, 101.16, 108.35, 117.49, 123.70, 126.17, 126.66, 127.51, 129.36 (double intensity), 129.52, 134.11, 143.92, 151.79, 155.48, 192.82; GC/MS (EI, 70 eV) m/e 352 (M^+), 252, 167, 144, 141. Anal. Calcd for $C_{22}H_{24}O_4$: C, 74.97; H, 6.86. Found: C, 74.87; H, 6.82.

3-[2-(1,3-Dioxan-2-yl)ethyl]-2-(phenyloxy)-2-cyclohexen-1-one (7b). Epoxide **6a** (1.1 g, 4.86 mmol) was treated with KH (2 drops, 40% in mineral oil), phenol (0.55 g, 5.83 mmol), and DMPU (0.99 mL) in THF (25 mL) according to the procedure described for preparation of **7a** (reaction time 42 h). The product was purified by silica gel chromatography (hexane/ethyl acetate (3:1)) to give **7b** (0.81 g, 55%): mp 71–72 °C; IR (film) 2960, 2860, 1680, 1635, 1595, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.3 (m, 1 H), 1.7–1.85 (m, 2 H), 2.0–2.2 (m, 3 H), 2.35 (m, 2 H), 2.5 (m, 4 H), 3.65 (dt, 2 H, J = 11.98 and 2.09 Hz), 4.05 (dd, 2 H, J = 10.61 and 5.04 Hz), 4.45 (t, 1 H, J = 5.09 Hz), 6.83 (d, 2 H,

(18) High-resolution mass spectra were obtained by Jeffrey Kiplinger, Philip Reiche, and Richard Ware.

(19) X-ray crystallographic analysis was conducted by Jon Bordner and Debra L. Decosta.

J = 7.93 Hz), 6.95 (m, 1 H), 7.25 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.26, 25.64, 26.05, 29.49, 32.29, 38.43, 66.76 (double intensity), 101.33, 114.66 (double intensity), 121.57, 129.38 (double intensity), 143.99, 151.57, 157.66, 193.03; GC/MS (EI, 70 eV) m/e 302 (M^+), 202, 167, 151. Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.49; H, 7.33. Found: C, 71.19; H, 7.34.

3-(4-Pentenyl)-2-(2-naphthalenyloxy)-2-cyclohexen-1-one (16a). Epoxide **6b** (1 g, 5.5 mmol) was treated with KH (0.06 g, 35% dispersion in oil), 2-naphthol (0.86 g, 6.0 mmol), and DMPU (0.66 mL, 4.5 mmol) in THF (7 mL) according to the procedure described for the preparation of **7a** (reaction time 16 h) to yield an oil, which, following chromatography on silica gel (hexane/ethyl acetate (10:1)), afforded **16a** as a light yellow solid (1.01 g, 60%): mp 47–48 °C; IR (carbon tetrachloride) 3060, 2930, 2860, 1685, 1625, 1595, 1510, 1460 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.2–2.6 (m, 12 H), 4.85–5.05 (m, 2 H), 5.6–5.8 (m, 1 H), 7.0–7.8 (m, 7 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.31, 26.37, 29.61, 31.06, 33.51, 38.43, 108.44, 115.14, 117.53, 123.82, 126.28, 126.75, 127.62, 129.47, 129.65, 134.22, 137.73, 143.99, 152.32, 155.82, 192.97; GC/MS (EI, 70 eV) m/e 306 (M^+), 265, 252, 237, 178; UV (MeOH) λ_{max} (ϵ) 226 (55063) nm. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.01; H, 7.20.

3-(4-Pentenyl)-2-(phenyloxy)-2-cyclohexen-1-one (16b). Epoxide **6b** (1 g, 5.5 mmol) was treated with phenol (0.56 g, 6.0 mmol), KH (0.06 g, 35% dispersion in oil), and DMPU (0.66 mL, 4.5 mmol) in THF (7 mL) according to the procedure described for the preparation of **7a** (reaction time 24 h). Chromatography of the resulting oil on silica gel (hexane/ethyl acetate (7:1)) gave **16b** (0.6 g, 43%): IR (carbon tetrachloride) 3080, 2930, 2870, 1685, 1635, 1590, 1490 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.5–2.7 (m, 12 H), 4.9–5.05 (m, 2 H), 5.65–5.85 (m, 1 H), 6.8–7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.14, 26.20, 29.43, 30.86, 33.38, 38.30, 114.52, 114.96 (double intensity), 121.44, 129.24 (double intensity), 137.66, 143.81, 151.98, 157.63, 192.93; GC/MS (EI, 70 eV) m/e 256 (M^+), 213, 163, 157, 145; UV (MeOH) λ_{max} (ϵ) 219 (11587), 244 (12380) nm. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.55; H, 7.77.

2-(2-Naphthalenyloxy)-3-oxo-1-cyclohexene-1-propanal (8a). The acetal **7a** (1.36 g, 3.85 mmol) was dissolved in acetic acid (80 mL, 80%) and stirred for 48 h at 65 °C. Product was extracted with methylene chloride, and the combined organic phases were washed with saturated sodium bicarbonate, water and brine and dried ($MgSO_4$). Solvent was removed on a rotary evaporator, and the crude product was purified by silica gel column chromatography (hexane/ethyl acetate (3:1)) to give aldehyde **8a** (0.97 g, 81%): mp 77.0–77.5 °C; IR (film) 3060, 2950, 2830, 2730, 1725, 1680, 1630, 1600, 1510 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.08 (m, 2 H), 2.52–2.58 (m, 8 H), 7.0 (s, 1 H), 7.2 (dd, 1 H, J = 8.94 and 2.51 Hz), 7.3 (t, 1 H), 7.44 (t, 1 H), 7.68 (d, 1 H, J = 7.98 Hz), 7.78 (d, 2 H, J = 8.83 Hz), 9.70 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.13, 24.20, 29.76, 38.24, 41.03, 108.41, 117.31, 123.97, 126.38, 126.72, 127.61, 129.51, 129.77, 134.12, 144.37, 149.90, 155.20, 192.62, 200.38; GC/MS (EI, 70 eV) m/e 294 (M^+), 209, 207, 205, 165, 141. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.26; H, 6.35.

2-(Phenyloxy)-3-oxo-1-cyclohexene-1-propanal (8b). The acetal **7b** (0.45 g, 1.5 mmol) was treated with acetic acid (30 mL, 80%) according to the procedure used for preparation of **8a**. Chromatography of the resulting oil on silica gel (hexane/ethyl acetate (3:1)) gave aldehyde **8b** (0.32 g, 87%): IR (film) 2950, 2730, 1720, 1680, 1630, 1590, 1490 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.06 (m, 2 H), 2.48–2.62 (m, 8 H), 6.79–7.28 (m, 5 H), 9.68 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.04, 24.09, 29.65, 38.17, 40.93, 114.45 (double intensity), 121.75, 129.39 (double intensity), 144.19, 149.75, 157.23, 192.73, 200.48; GC/MS (EI, 70 eV) m/e 244.1 (M^+), 215, 202, 173, 107, 94, 77; HRMS calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1083.

(*E*)-5-[2-(2-Naphthalenyloxy)-3-oxo-1-cyclohexen-1-yl]-2-pentenoic Acid, Ethyl Ester (1c). Sodium hydride (0.037 g, 1.55 mmol) and DMSO (1.6 mL) were warmed to 55 °C and stirred for 60 min under a nitrogen atmosphere, after which a solution of (carbethoxymethyl)triphenylphosphonium bromide (0.641 g, 1.5 mmol) in DMSO (1.6 mL) was added slowly. During the addition, the color of the mixture changed to dark red. The resulting solution was stirred at 65 °C for 30 min, cooled to room temperature, and then transferred via cannula to a solution of the aldehyde **8a** (0.22 g, 0.747 mmol) in DMSO (2 mL). The reaction mixture was stirred for an additional 30 min at room temperature, after which it was poured into water (20 mL) and the aqueous phase was extracted with methylene chloride. The combined organic phases were washed with water and brine and dried ($MgSO_4$). Solvent was removed, and the product was purified by chromatography on silica gel (hexane/ethyl acetate (3:1)) to afford **1c** (0.23 g, 85%): mp 75.5–76.0 °C; IR (film) 3060, 2950, 1720, 1685, 1655, 1630, 1600, 1510, 1465 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.23 (t, 3 H, J = 7.13 Hz), 2.00–2.60 (m, 10 H), 4.13 (q, 2 H, J = 7.15 Hz), 5.78 (dt, 1 H, J = 15.62 and 1.47 Hz), 6.83–6.91 (dt, 1 H, J = 15.62 and 6.57 Hz), 6.98 (d, 1 H, J = 2.46 Hz), 7.20 (dd, 1 H, J = 8.92 and 2.54 Hz), 7.25–7.45 (m, 2 H), 7.65 (d, 1 H, J = 7.81 Hz) and 7.78 (d, 2 H, J = 9.01 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.07 (1°), 22.06 (2°), 29.45 (2°, double intensity), 29.93 (2°), 38.26 (2°), 60.14 (2°), 108.38 (3°), 117.34 (3°), 122.18 (3°), 123.85 (3°), 126.27 (3°), 126.70 (3°), 127.55 (3°), 129.44 (4°), 129.67 (3°), 134.09 (4°), 144.29 (4°), 146.74 (3°), 150.04 (4°), 155.33 (4°), 166.06 (4°), 192.66 (4°); GC/MS (EI, 70 eV) m/e 364 (M^+), 334, 319, 275, 263, 251, 250; UV (MeOH) λ_{max} (ϵ) 225 12083) nm. Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.83; H, 6.76.

5-[3-Oxo-2-(phenyloxy)-1-cyclohexen-1-yl]-2-pentenoic Acid, Ethyl Ester (13a). Aldehyde **8b** (0.31 g, 1.27 mmol) was treated with sodium hydride (0.067 g, 2.78 mmol), and (carbethoxymethyl)triphenylphosphonium bromide (1.09 g, 2.54 mmol) in DMSO (6 mL) according to the procedure described for the preparation of **1c** to give an oil that after chromatography on silica gel (hexane/ethyl acetate (3:1)) afforded **13a** (0.29 g, 73%): mp 54.5–55.5 °C; IR (film) 3060, 2965, 1720, 1685, 1655, 1590, 1490 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.28 (t, 3 H, J = 7.13 Hz), 2.08 (m, 2 H), 2.30–2.60 (m, 8 H), 4.17 (q, 2 H, J = 7.13 Hz), 5.80 (d, 1 H, J = 15.6 Hz), 6.75–7.05 (m, 4 H), 7.25 (t, 2 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.84, 21.76, 29.10, 29.56, 37.97, 59.81, 114.25 (double intensity), 121.33, 121.82, 129.07, 143.66, 146.63, 149.70, 157.22, 165.73, 192.43; GC/MS (EI, 70 eV) m/e 314 (M^+), 285, 269, 201; UV (MeOH) λ_{max} (ϵ) 243 (6025), 214 (8662) nm. Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.20; H, 7.08.

Pyrex-Filtered Irradiation of 1c: 1,2,3,4,5,6-Hexahydro-4-oxo-(4aα,5β,6α,6aα,12cβ)-12b*H*-4a,6a-epoxy-5,12c-ethanobenzo[*c*]phenanthrene-6-carboxylic Acid, Ethyl Ester (9a). Compound **1c** (0.1082 g, 2.97 mmol) was dissolved in dry toluene (216 mL). Argon gas was bubbled through the solution for 30 min after which the reaction mixture was irradiated through Pyrex for 35 min at room temperature.[10] Solvent was removed under reduced pressure, and the resulting product was purified by column chromatography on silica gel (carbon tetrachloride/ethyl acetate (20:1)) to give **9a** (0.092 g, 85%): mp 116.5–117.5 °C; IR (film) 3060, 2950, 2878, 1725 (br), 1630, 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.22 (t, 3 H, J = 7.11 Hz), 1.60–2.80 (m, 10 H with overlapping doublet at 2.58, J = 3.88 Hz), 3.00 (m, 1 H), 3.50 (s, 1 H), 4.11 (q, 2 H, J = 7.06 Hz), 6.35 (d, 1 H, J = 9.88 Hz), 6.50 (d, 1 H, J = 9.96 Hz), 7.25 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.26 (1°), 20.43 (2°), 25.60 (2°), 30.90 (2°), 37.07 (2°), 39.31 (2°), 47.77 (3°), 49.79 (4°), 51.60 (3°), 60.43 (3°), 60.54 (2°), 88.87 (4°), 97.61 (4°), 126.47 (3°), 126.75 (3°), 126.93 (3°), 127.77 (3°), 128.53 (3°), 130.38 (3°), 133.72 (4°), 134.87 (4°), 172.03 (4°), 207.15 (4°); GC/MS (EI, 70 eV) m/e 364 (M^+), 319, 277, 250, 237; UV (MeOH) λ_{max} (ϵ) 267 (2028), 227 (11990) nm. Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.81; H, 6.64. Found: C, 76.12; H, 6.67.

Irradiation of 1c with a 366-nm Light Source. A solution of **1c** (0.033 g, 0.09 mmol) in methanol/toluene (1:1, 33 mL) was irradiated for 5 h at room temperature through Pyrex with a 366-nm light source.[13] The solvent was removed under reduced pressure, and the reaction products were separated by silica gel column chromatography (carbon tetrachloride/ethyl acetate (30:1)), followed by carbon tetrachloride/ethyl acetate (20:1)) to provide **3c** (0.0148 g, 45%), **11** (0.0078 g, 24%), and **12** (0.0076 g, 23%).

8,9,10,11-Tetrahydro-8-oxo-7a,11a-propanobenzo[*b*]naphtho[1,2-*d*]furan-14-acetic acid, ethyl ester (3c): mp 112.5–113 °C; IR (film) 3060, 2955, 2860, 1725, 1630, 1605, 1585, 1465 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.22–2.84 (m, 16 H; with overlapping triplet at 1.25, J = 7.14 Hz), 4.13 (q, 2 H, J = 7.13 Hz), 7.16 (d, 1 H, J = 8.8 Hz), 7.30 (t, 1 H, J = 7.54 Hz), 7.45 (t,

1 H, J = 8.4 Hz), 7.67 (d, 1 H, J = 8.89 Hz), 7.78 (d, 1 H, J = 6.5 Hz), 7.82 (d, 1 H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.14 (1°), 18.63 (2°), 30.33 (2°), 32.99 (2°), 33.36 (2°), 35.91 (2°), 37.37 (2°), 44.26 (3°), 60.46 (2°), 61.39 (4°), 99.05 (4°), 111.82 (3°), 121.51 (3°), 122.85 (3°), 123.12 (4°), 126.68 (3°), 129.44 (3°), 129.49 (4°), 129.97 (3°), 130.32 (4°), 156.32 (4°), 172.65 (4°), 208.60 (4°); GC/MS (EI, 70 eV) m/e 364 (M^+), 319, 262, 221; UV (MeOH) λ_{max} (ε) 231 (83 269), 210 (36 002) nm; HRMS calcd for $C_{23}H_{24}O_4$ 364.1674, found 364.1663. Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.69; H, 6.57.

5-(8,9,10,11-Tetrahydro-8-oxobenzo[*b*]naphtho[1,2-*d*]furan-11a(7a*H*)-yl)-2-pentenoic acid, ethyl ester (11): IR (film) 3060, 2940, 1720, 1655, 1630, 1600, 1580, 1520 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.24 (t, 3 H, J = 7.13 Hz), 1.73–2.70 (m, 10 H), 4.13 (q, 2 H, J = 7.14 Hz), 4.69 (s, 1 H), 5.69 (d, 1 H, J = 15.7 Hz), 6.82 (dt, 1 H, J = 15.73 and 5.98 Hz), 7.19 (d, 1 H, J = 8.83 Hz), 7.33 (t, 1 H, J = 7.46 Hz), 7.46 (t, 1 H, J = 7.65 Hz), 7.74 (d, 1 H, J = 8.77 Hz), 7.77 (d, 1 H, J = 8.33 Hz), 7.84 (d, 1 H, J = 8.39 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.15 (1°), 19.23 (2°), 27.21 (2°), 33.26 (2°), 36.89 (2°), 37.70 (2°), 55.07 (4°), 60.13 (2°), 89.67 (3°), 112.25 (3°), 120.32 (4°), 121.98 (3°), 121.63 (3°), 123.28 (3°), 127.11 (3°), 129.67 (3°), 130.05 (4°), 160.39 (4°), 130.77 (3°), 147.58 (3°), 157.58 (4°), 166.28 (4°), 208.39 (4°); GC/MS (EI, 70 eV) m/e 364 (M^+), 319, 262, 207; UV (MeOH) λ_{max} (ε) 232 (45 416), 211 (28 034) nm; HRMS calcd for $C_{23}H_{24}O_4$ 364.1674, found 364.1684.

Compound 12: mp 137.5–139 °C; IR (film) 2950, 2875, 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.19 (t, 3 H, J = 7.14 Hz), 1.30–2.55 (m, 10 H), 3.0–3.13 (m, 2 H, with overlapping doublet at 3.02, J = 4.76 Hz), 4.0–4.12 (m, 2 H), 4.17 (s, 1 H), 5.87 (d, 1 H, J = 9.91 Hz), 6.44 (d, 1 H, J = 9.96 Hz), 6.98–7.19 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.31 (1°), 20.07 (2°), 29.55 (2°), 31.30 (2°), 37.13 (2°), 42.22 (2°), 46.90 (3°), 58.04 (3°), 60.15 (4°), 60.58 (2°), 65.33 (4°), 84.52 (4°), 86.57 (3°), 122.40 (3°), 126.54 (3°), 126.93 (3°), 128.06 (3°), 128.38 (3°), 129.55 (3°), 131.11 (4°), 135.90 (4°), 171.06 (4°), 209.57 (4°); GC/MS (EI, 70 eV) m/e 364 (M^+), 319, 277, 262, 237, 207; UV (MeOH) λ_{max} (ε) 268 (4327), 221 (27 181) nm. Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.57; H, 6.66.

Irradiation of 13a: 5-(1,3,4,9a-Tetrahydro-1-oxo-4a-(2*H*)-dibenzofuranyl)-2-pentenoic Acid, Ethyl Ester (14a). Compound **13a** (0.112 g, 0.36 mmol) was dissolved in dry toluene (233 mL) and irradiated for 95 min through Pyrex.[10] The solvent was removed on a rotary evaporator, and the resulting oil was purified by silica gel chromatography (carbon tetrachloride/ethyl acetate (20:1), followed by carbon tetrachloride/ethyl acetate (10:1)) to afford **14a** (69.4 mg, 62%): mp 73.5–74.5 °C; IR (film) 3055, 2940, 1735, 1720, 1650, 1610, 1590, 1455 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.27 (t, 3 H, J = 7.08 Hz), 1.55–2.62 (m, 10 H), 4.15 (q, 2 H, J = 7.08 Hz), 4.56 (s, 1 H), 5.77 (dt, 1 H, J = 15.75 and 1.59 Hz), 6.72–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.19 (1°), 20.37 (2°), 26.84 (2°), 32.50 (2°), 38.28 (2°), 39.45 (2°), 53.27 (4°), 60.18 (2°), 89.77 (3°), 110.46 (3°), 121.60 (3°), 121.66 (3°), 122.60 (3°), 129.07 (3°), 130.43 (4°), 147.65 (3°), 159.40 (4°), 166.35 (4°), 208.09 (4°); GC/MS (EI, 70 eV) m/e 314 (M^+), 269, 240, 227, 212; UV (MeOH) λ_{max} (ε) 272 (2420), 202 (26 030) nm; HRMS calcd for $C_{19}H_{22}O_4$ 314.1518, found 314.1520. Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.77; H, 7.08.

1,2,3,4-Tetrahydro-4-oxo-4a,9b-propanodibenzofuran-12-acetic Acid, Ethyl Ester (15a). Compound **14a** was dissolved in benzene/methanol (1:1, 16 mL), and sodium carbonate (0.1694 g, 0.16 mmol) was added. The reaction mixture was stirred at room temperature for 3 h after which the solution was filtered and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel to afford **15a** (9.3 mg, 57%): IR (film) 2950, 2875, 1730, 1595, 1480, 1460 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.25 (t, 3 H, J = 7.14 Hz), 1.40–2.85 (m, 13 H), 4.12 (q, 2 H, J = 7.16 Hz), 6.82–7.18 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.16 (1°), 19.26 (2°), 30.02 (2°), 33.23 (2°), 33.93 (2°), 36.65 (2°), 40.29 (2°), 43.78 (3°), 60.12 (4°), 60.48 (2°), 98.61 (4°), 109.37 (3°), 121.49 (3°), 122.61 (3°), 128.47 (3°), 134.00 (4°), 158.91 (4°), 172.72 (4°), 208.71 (4°); GC/MS (EI, 70 eV) m/e 314.75 (M^+), 269.70, 227.50, 212.50, 199.45; UV (MeOH) λ_{max} (ε) 277 (2008), 202 (10 591) nm; HRMS calcd for $C_{19}H_{22}O_4$ 314.1518, found 314.1505.

Irradiation of 1d. A solution of **1d** (100 mg, 0.34 mmol) in dry toluene (200 mL) was irradiated through Pyrex at 110 °C for 65 min.[10] The solvent was removed under reduced pressure, and the reaction products were isolated by silica gel column chromatography to afford **9b** and **3d** (5.13:1 by ^{1}H NMR analysis). Product **9b** was isolated in purified form by crystallization with ethyl ether: mp 125–126 °C; IR (film) 2940, 2875, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.49–2.73 (m, 13 H), 3.47 (s, 1 H), 6.28 (d, 1 H, J = 9.9 Hz), 6.40 (d, 1 H, J = 9.9 Hz), 7.17–7.26 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.30, 26.32, 30.95, 36.66, 37.11, 39.42, 42.67, 49.36, 60.76, 87.86, 98.37, 126.64 (double intensity), 127.47, 128.16, 129.01, 129.30, 134.72, 134.93, 208.65; GC/MS (EI, 70 eV) m/e 292 (M^+), 237, 233, 218, 205; UV (MeOH) λ_{max} (ε) 264 (5116), 218 (16 724), 213 (15 715) nm. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.21; H, 6.79.

Irradiation of 16a. A solution of **16a** (200 mg, 0.065 mmol) in dry toluene (200 mL) was degassed with argon for 30 min and irradiated with Pyrex-filtered light for 55 min at reflux temperature.[10] The solvent was evaporated under reduced pressure, and the products were isolated by chromatography on silica gel (hexane/ethyl acetate (10:1)) to give **17a** (32 mg, 16%), **18a** (29 mg, 14.5%), and **18b** (104 mg, 52%).

6-(2-Naphthalenyloxy)[6.3.0.0^{1,6}]undecan-5-one (17a): IR (film) 3060, 2940, 2860, 1720, 1635, 1605, 1515, 1470 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.23–1.34 (m, 1 H), 1.57–1.96 (m, 7 H), 2.02–2.15 (m, 2 H), 2.35–2.51 (m, 2 H), 2.59–2.66 (m, 2 H), 2.84 (dd, 1 H, J = 13.66 and 8.93 Hz), 6.82 (d, 1 H, 2.48 Hz), 7.09 (dd, 1 H, J = 8.88 and 2.53 Hz), 7.26–7.44 (m, 2 H), 7.63–7.75 (m, 3 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.73 (2°), 25.93 (2°), 31.38 (2°), 32.45 (2°), 32.68 (2°), 34.84 (2°), 36.14 (3°), 37.75 (2°), 57.29 (4°), 80.75 (4°), 110.77 (3°), 119.33 (3°), 123.71 (3°), 126.18 (3°), 126.81 (3°), 127.48 (3°), 129.01 (4°), 129.25 (3°), 134.09 (4°), 153.84 (4°), 210.47 (4°); GC/MS (EI, 70 eV) m/e 306 (M^+), 235, 221, 163; UV (MeOH) λ_{max} (ε) 272 (12 187), 228 (66 573) nm; HRMS calcd for $C_{21}H_{22}O_2$ 306.1620, found 306.1621.

11a-(4-Pentenyl)-9,10,11,11a-tetrahydrobenzo[*b*]naphtho[1,2-*d*]furan-8(7a*Hα*)-one (18a, trans): IR (film) 3400, 3060, 2940, 2860, 1735, 1625, 1605, 1585, 1520, 1455 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20–3.0 (m, 12 H), 4.77–4.85 (m, 2 H), 4.98 (s, 1 H), 5.47–5.68 (m, 1 H), 7.25 (d, 1 H, J = 8.76 Hz), 7.31–7.51 (m, 2 H), 7.72 (d, 1 H, J = 8.89 Hz), 7.82 (d, 2 H, J = 8.25 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 23.22 (2°), 23.42 (2°), 31.15 (2°), 31.95 (2°), 33.84 (2°), 38.75 (2°), 54.64 (4°), 94.26 (3°), 113.21 (3°), 114.76 (2°), 122.94 (3°), 123.33 (3°), 126.61 (3°), 126.84 (4°), 129.10 (3°), 129.67 (3°), 130.12 (4°), 131.00 (4°), 137.96 (3°), 156.39 (4°), 203.71 (4°); GC/MS (EI, 70 eV) m/e 306 (M^+), 238, 237, 209, 181; UV (MeOH) λ_{max} (ε) 230 (59 037), 220 (23 676) nm; HRMS calcd for $C_{21}H_{22}O_2$ 306.1620, found 306.1643.

11a-(4-Pentenyl)-9,10,11,11a-tetrahydrobenzo[*b*]naphtho[1,2-*d*]furan-8(7a*Hβ*)-one (18b, cis): IR (film) 3400, 3070, 2935, 2860, 1730, 1625, 1600, 1580, 1520, 1460 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.16 (m, 1 H), 1.47 (m, 1 H), 1.70–2.70 (m, 10 H), 4.69 (s, 1 H), 4.87–4.97 (m, 2 H), 5.55–5.76 (m, 1 H), 7.19 (d, 1 H, J = 8.78 Hz), 7.32 (m, 1 H), 7.46 (m, 1 H), 7.71 (d, 1 H, J = 10.74 Hz), 7.82 (m, 2 H); ^{13}C NMR (CD_3COCD_3, 50.3 MHz) δ 20.00 (2°), 24.46 (2°), 33.80 (2°), 34.48 (2°), 37.57 (2°), 39.65 (2°), 55.78 (4°), 90.57 (3°), 112.85 (3°), 115.04 (4°), 122.41 (3°), 122.79 (4°), 123.74 (3°), 127.63 (3°), 130.25 (3°), 131.05 (3°), 131.16 (4°), 131.20 (2°), 139.12 (3°), 158.38 (4°), 208.22 (4°); GC/MS (EI, 70 eV) m/e 306 (M^+), 238, 237, 209, 181, 152; UV (MeOH) λ_{max} (ε) 232 (58 018), 211 (16 771) nm; HRMS calcd for $C_{21}H_{22}O_2$ 306.1620, found 306.1597.

Irradiation of 16b. A solution of **16b** (200 mg, 0.78 mmol) in toluene (220 mL) was irradiated with Pyrex-filtered light for 1.5 h at room temperature.[10] Solvent was removed under reduced pressure, and the resulting oil was purified by column chromatography on silica gel (hexane/ethyl acetate (20:1)) to give **17b** (148 mg, 78%) and **19** (26.9 mg, 13.5%).

6-(Phenyloxy)[6.3.0.0^{1,6}]undecan-5-one (17b): mp 44.5–45.5 °C; IR (carbon tetrachloride) 2950, 1710, 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.25–1.36 (m, 2 H), (9246) nm. (m, 7 H), 2.30–2.45 (m, 2 H), 2.54–2.62 (m, 2 H), 2.70–2.76 (d, 1 H, J = 13.61 Hz), 2.73–2.81 (d, 1 H, J = 13.60 Hz), 6.71–6.77 (m, 2 H), 6.86–6.94 (m, 1 H), 7.15–7.25 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.56 (2°), 25.76 (2°), 31.23 (2°), 32.30 (2°), 32.47 (2°), 34.45 (2°), 35.89 (3°), 37.59 (2°), 57.07 (4°), 80.25 (4°), 116.57 (3°, double intensity),

120.83 (3°), 128.97 (3°, double intensity), 155.93 (2°), 210.26 (4°); GC/MS (EI, 70 eV) m/e 256 (M^+), 135, 119, 107, 91; UV (MeOH) λ_{max} (ϵ) 270 (1071), 221 (8770), 202 (9246) nm. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.68; H, 7.79.

9b-(4-Pentenyl)-2,3,4a,9b-tetrahydro-4(1*H*)-dibenzofuran (19): IR (film) 3460, 3070, 2930, 2865, 1745, 1650, 1615, 1590, 1460 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.25-1.42 (m, 4 H), 1.86-2.06 (m, 5 H), 2.41-2.51 (m, 3 H), 4.80 (s, 1 H), 4.84-4.92 (m, 2 H), 5.54-5.75 (m, 1 H), 6.90-7.27 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.2 (2°), 22.99 (2°), 28.77 (2°), 29.98 (2°), 33.67 (2°), 38.99 (2°), 52.89 (4°), 93.86 (3°), 111.46 (3°), 114.86 (2°), 121.32 (3°), 123.16 (3°), 128.39 (3°), 134.94 (4°), 137.98 (3°), 158.35 (4°), 203.43 (4°); GC/MS (EI, 70 eV) m/e 256 (M^+), 187, 159; UV (MeOH) λ_{max} (ϵ) 273 (2580), 202 (11 157) nm; HRMS calcd for $C_{17}H_{20}O_2$ 256.1483, found 256.1464.

Acknowledgment. J.P.D. gratefully acknowledges the support of NIH (GM 37939) and the Camille and Henry Dreyfus Foundation (for funds contributed toward the purchase of an NMR).

Supplementary Material Available: Proton NMR spectra for **18a** and **18b**; carbon NMR spectra for compounds **8b**, **11**, **15a**, **17a**, and **19**; and full details on X-ray crystallographic analyses including tables of coordinates, anisotropic temperature factors, distances, and angles (41 pages). Ordering information is given on any current masthead page.

Preparation and 3-Aza-Cope Rearrangement of *N*-Alkyl-*N*-allyl Enamines

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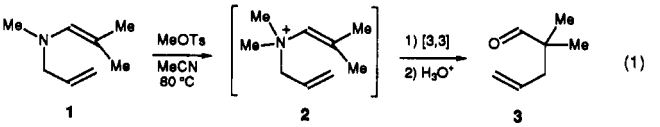
Received March 22, 1991

The [3,3] charge-accelerated rearrangement of *N*-allyl-*N*-isobutyl enamine substrates to γ,δ-unsaturated imine products and subsequent reduction to the corresponding *N*-alkyl δ,ϵ-unsaturated amines is reported. Several routes to the *N*-allyl-*N*-isobutyl enamines were established for the enamine prepared from isobutyraldehyde. With use of the most efficient route developed, enamines derived from butanal, 2-phenylpropanal, cyclohexanone, and cyclopentanone were prepared in 58 to 92% overall yield in three steps from allylamine. In the case of butanal, the *E* isomer was formed exclusively, while the enamine from 2-phenylpropanal was prepared with an *E* to *Z* selectivity of 86:14. Heating these *N*-allyl-*N*-isobutyl enamines in refluxing dioxane with 0.5 equiv of HCl produced [3,3] rearrangement for substrates derived from isobutyraldehyde, 2-phenylpropanal, and cyclohexanone; the enamines of *n*-butanal and cyclopentanone were found to react through alternate pathways.

The study of the Claisen rearrangement, the [3,3] sigmatropic shift of allyl vinyl ethers, has provided many valuable contributions to the areas of mechanistic and synthetic chemistry.[1] Several features, including the convergent nature of the allyl enol ether preparation and subsequent C-C bond formation, have contributed to the extensive use of this reaction in organic synthesis. The products of this pericyclic process, γ,δ-unsaturated carbonyl compounds, are valuable synthons with different functionality at each terminus. Because of the different reactivity at each end, subsequent synthetic elaboration or incorporation of this fragment into a larger target molecule can be efficiently accomplished.

The nitrogen analogue of the Claisen rearrangement, the 3-aza-Cope rearrangement of **1**, has been reported to undergo thermally induced [3,3] sigmatropic rearrangement to the corresponding imine at 250 °C, and subsequent hydrolysis of the imine produced **3**.[2] Several approaches to rate enhancement of this transformation have been made through the electronic modification of the enamine functionality. Thermal rearrangement of the aniline-derived *N*-phenyl-*N*-allyl enamine was found to occur at a somewhat reduced temperature of 205 °C.[2] Rearrangement at lower reaction temperatures could be achieved by substrates with oxygen substituents at C-2. For example, ketene *N,O*-acetals underwent thermal sigmatropic transformation at 180 °C,[3] and allylamide enolates were found to rearrange at 130 °C.[4] The temperatures necessary for rearrangement to occur have been a major limiting feature of the 3-aza-Cope rearrangement. At the elevated temperatures for thermal rearrangement, technical difficulties commonly arise in setting up the reaction, monitoring its progress, and workup of the reaction mixture. Typically, in these cases the [3,3] transformation must be incorporated into multistep synthetic sequences early, so as not to disturb sensitive functionality.

Methods of promoting the aza-Cope rearrangement at even lower temperatures have involved the formation of cationic quaternary nitrogen centers. As shown in eq 1, one way to access an intermediate such as **2** has been accomplished by methylation of the *N*-alkyl-*N*-allyl enamine **1**. Under the 80 °C conditions for methylation of



1 2 3 (1)

allyl enamines, which has only been successfully performed on enamine substrates formed from 2-substituted aldehydes, rearrangement also occurred and hydrolytic workup of the reaction mixture produced **3**.[5] A modification of the methylation procedure, methylation of an *N*-allylimine

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