6 (12.5 mg), 7 (3.0 mg), and 8 (4.2 mg). Compound 6: oil; ^{1}H NMR ($CDCl_3$) δ 3.70 (m, H-13, H-17), and Me's at 0.87, 0.85 (A = 2), and 0.84; ^{13}C NMR ($CDCl_3$, 75 MHz) see Table I; MS (20 eV), m/z 304 ($M^+ - H_2O$), 289 ($M^+ - CH_5O$), 136 (base). Compound 7: oil; ^{1}H NMR ($CDCl_3$) δ 4.70 (m, H-13), 2.95 (H-17), and Me's at 0.91, 0.87, and 0.85 (A = 2); ^{13}C NMR ($CDCl_3$, 75 MHz), see Table I; MS (20 eV), m/z 319 ($M^+ - OH$), 318 ($M^+ - H_2O$), 303 ($M^+ - CH_5O$), 136 (base). Compound 8: oil; ^{1}H NMR ($CDCl_3$) δ 4.15 (m, H-13) and Me's at 0.87, 0.85 (A = 2), and 0.84; ^{13}C NMR ($CDCl_3$, 75 MHz), see Table I, MS (20 eV), m/z 319 ($M^+ - OH$), 318 ($M^+ - H_2O$), 304 ($M^+ - CH_4O$), 123 (base).

Hydrogenation of Suvanine (1b) to Tetrahydrofuran 11. A solution of suvanine (10.0 mg, 0.019 mmol) and Pd/C (1 mg) in EtOAc (5 mL) was stirred under H_2 (1 atm) for 48 h. The product was filtered through celite, and the solvent was removed to give 11 (10.1 mg, 99%): ^{1}H NMR ($CDCl_3$) δ 6.97 (br s, 3 H, D_2O exchangeable), 6.66 (br s, 1 H, D_2O exchangeable), 6.18 (d, J = 5), 3.86 (m, 2 H, J = 7, 13), 3.70 (dd, 1 H, J = 8, 13), 3.34 (dt, 1 H, J = 7, 13), 2.50 (m, 1 H), 2.40 (m, 1 H), 2.28 (m, 1 H), 2.03 (m, 2 H), 1.80 (br d), 1.67 (dd), 1.54 (m), 1.36 (dd), 1.29 (dd), 1.17 (dd), 1.06 (m), 1.00 (s, 3 H), 0.89 (m, 1 H), 0.87 (s, 3 H), 0.85 (s, 3 H), 0.79 (s, 3 H).

X-ray Procedures. A colorless crystal of dimensions 0.20 × 0.24 × 0.52 mm was used for data collection on an Enraf-Nonius CAD4 diffractometer equipped with a Mo Kα radiation (wavelength = 0.71073 Å) and a graphite monochromator. Crystal data are as follows: $C_{21}H_{38}O_2$, monoclinic space group $P2_1$, a = 10.903 (2), b = 7.807 (4), and c = 11.491 (2) Å, β = 99.33 (2)°, V = 965.2 (9) Å^3, Z = 2, D_c = 1.110 g cm^{-3}, μ(Mo Kα) = 0.89 cm^{-1}, T = 21 °C. Intensity data were collected by Ω-2θ scans within one quadrant having 1° < θ < 27° by using varying scan speeds of 0.45–4.0°/min in order to measure all significant data with I = 50$\sigma(I)$. A maximum of 120 s was spent on any single scan. Data reduction included corrections for background, Lorentz, and polarization effects. Of 2257 unique data, 1416 had $I > 2\sigma(I)$ and were used in the refinement. The absolute configuration was not determined. The structure was solved by using MULTAN78[14] and refined by full-matrix least squares, treating non hydrogen atoms anisotropically. H atoms were located by difference maps. The hydroxyl hydrogen atoms were isotropically refined, while other H atoms were placed in calculated positions with C-H 0.95 Å, and B = 5.0 Å^2. Convergence was achieved with R = 0.048 and R_w = 0.043 for 216 variables, extinction coefficient = 7.7(15) × 10^{-7}, and maximum residual density 0.14 e Å^{-3}. Complete coordinates and anisotropic thermal parameters are in Tables 3S–5S, supplementary material.

Acknowledgment. Partial research support to P.C. and to D.J.F. was from NOAA, National Sea Grant College Program, Department of Commerce, University of California, project number R/MP-33 (PC) and R/MP-30 (DJF). L.V.M. and M.R.K. were Sea Grant Trainees. The U.S. Government is authorized to produce and distribute reprints for governmental purposes. Other support to D.J.F. was from the NIH (Grant AI-11969) and Allergan Pharmaceuticals. A grant to P.C. from the University Research Expeditions Program supported field work in Fiji. P.C. is also grateful for the cooperation of the Fiji Government. We thank Professor Pat Bergquest (University of Auckland) and Professor Gerald J. Bakus (University of Southern California) for sponge taxonomy information.

Supplementary Material Available: Figures of the ^{13}C NMR spectrum of 1c and ^{1}H–^{13}C COSY spectrum of 1b and tables containing bond distance and angles, torsion angles, and coordinates and anisotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

(14) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*; University of York and University of Louvain.

Photorearrangements of Carbomethoxy-Substituted Cyclohexadienones in Neutral Media

Chris A. Broka

Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801-3731

Received June 15, 1987

The photochemistry of several 2-carbomethoxy-3-keto-$\Delta^{1,4}$-hexahydronaphthalenes has been investigated. Unlike analogous bicyclic cyclohexadienones lacking a 2-carbomethoxy substituent, these systems do not undergo normal type-A photorearrangements upon irradiation in nonprotonating solvents. Instead, they afford exocyclic hydroazulenone olefins resulting from proton loss from their angular substituents as well as hydroxy ketones and decarbomethoxylated ethers which have been shown to arise from their derived Zimmerman–Schuster zwitterions by way of intramolecular processes involving attack of the carbomethoxy group upon the electrophilic C-9 center. The behavior of these systems is contrasted with that of a 4-carbomethoxy-substituted dienone and a monocyclic, 2-carbomethoxy-substituted dienone, both of which were found to undergo the expected type-A photorearrangements under neutral conditions.

In connection with efforts directed toward the synthesis of methyl homodaphniphyllate (1)[1,2] we have had occasion to examine the photochemistry of several carbomethoxy-substituted 2,5-cyclohexadienones in neutral media. A brief retrosynthetic analysis of this alkaloid is outlined in Scheme I.

Implementation of this approach requires a fairly general entry into hydroazulenone aldehydes of the type exemplified by 2. Since 2 might be obtainable through Claisen rearrangement of enol ether 3 we were motivated to explore routes to such compounds. Our attention was drawn to the work of Caine[3] who demonstrated that irradiation of the bicyclic 2-carboxycyclohexadienone 4 in anhydrous

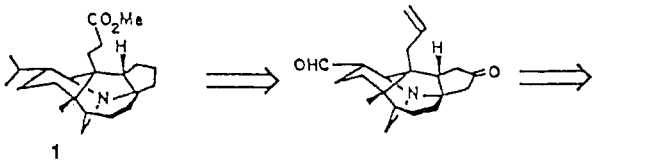
(1) Toda, M.; Niwa, H.; Irikawa, H.; Hirata, Y.; Yamamura, S. *Tetrahedron* **1974**, *30*, 2683.

(2) The synthesis of 1 has recently been achieved by Heathcock et al. (Heathcock, C. H.; Davidson, S. K.; Mills, S.; Sanner, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 5650).

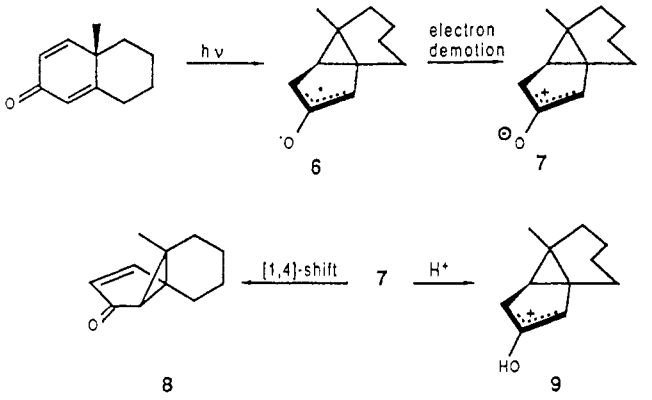
(3) (a) Caine, D.; DeBardelen, J. F., Jr.; Dawson, J. B. *Tetrahedron Lett.* **1966**, *3627*. (b) Caine, D.; Brake, P. F.; DeBardelen, J. F.; Dawson, J. B. *J. Org. Chem.* **1973**, *38*, 967.

0022-3263/88/1953-0575$01.50/0

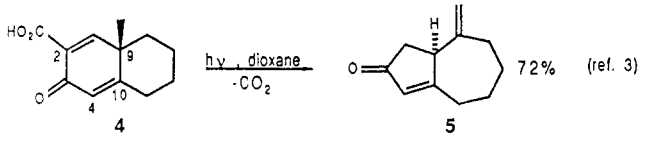
Scheme I



Scheme II

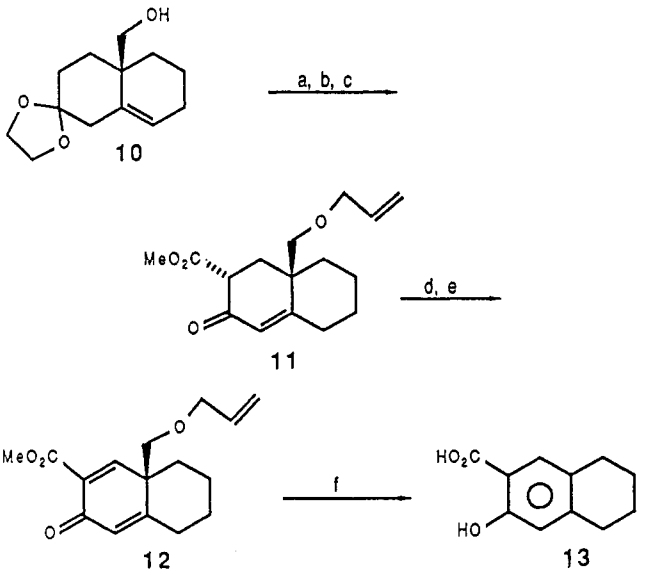


dioxane gave rise to **5** in good yield. We reasoned that **3** might be prepared similarly.



Irradiation of cross-conjugated cyclohexadienones[4] (Scheme II) yields products whose origin Zimmerman[5] has traced to zwitterionic intermediates[6] exemplified by **7**. Intermediates **7** were postulated by Zimmerman to result, upon ($\pi^* \rightarrow$ n) electron demotion, from the diradical species **6**, itself derived from the n–π^* triplet excited state of the starting material. In neutral aprotic media **7** generally rearranges to the cyclopropyl ketone (lumiketone) **8**, whereas under acidic conditions it undergoes protonation to give **9**, followed by S_N2 cleavage of one of the lateral bonds of the cyclopropane ring to afford hydroazulenone or spirocyclic products. The fact that **4** gives rise to the

Scheme III[a]



[a] (a) allyl bromide, KH, THF; (b) H_3^+; (c) LDA, $NCCO_2Me$, THF, HMPA; (d) KH, PhSeCl, THF, 0 °C; (e) H_2O_2, CH_2Cl_2, 0 °C; (f) ester hydrolysis.

hydroazulenone **5** on irradiation under neutral conditions, instead of to a cyclopropyl ketone or to secondary photoproducts thereof, was easily explained as being due to intramolecular protonation of the zwitterionic intermediate by the C-2 carboxy group with the resulting oxyallyl cation losing a proton from the angular methyl group. Formation of the 5/7-fused product, as opposed to a spirocyclic enone, was attributed to an electronic directing effect exerted by the C-2 carboxy group.

We have found that exocyclic olefins related to **5** are also obtained upon irradiation of the methyl esters of **4** and of analogous compounds. Moreover, this is the case under *neutral* as well as acidic reaction conditions. The present report describes our studies concerning the scope and mechanism of this interesting transformation.

Results and Discussion

The cyclohexadienone **12** was easily prepared from the known alcohol **10**[7] by the method outlined in Scheme III.

Both the carbomethoxylation (using the procedure of Mander[8]) and the subsequent conversion of **11** into **12** by selenation and oxidation[9] were accomplished without difficulty. However, all attempts to effect the hydrolysis of **12** to its corresponding acid failed, giving instead the phenol **13**. It seems likely that the acid is being produced in these reactions but that, given the driving force provided by aromatization and the relative availability of the allyloxy oxygen lone pairs, it rapidly expels the angular substituent.[10]

(4) For several excellent reviews of this subject, see: (a) Kropp, P. J. *Org. Photochem.* **1967**, *1*, 1. (b) Zimmerman, H. E. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 1. (c) Barton, D. H. R. *Helv. Chim. Acta* **1975**, *42*, 2604. (d) Schaffner, K.; Demuth, M. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed; Academic: New York, 1980; Vol. 3, Chapter 5.

(5) (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1961**, *83*, 4487. (b) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527.

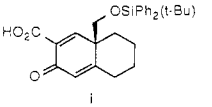
(6) The status of species such as **6** and **7** as true *intermediates* (i.e., local energy minima along the reaction coordinate) is, in general, uncertain.

(7) Dreiding, A. S.; Tomasewski, A. J. *J. Am. Chem. Soc.* **1955**, *77*, 411.

(8) Mander, L. N.; Sethi, S. P. *Tetrahedron Lett.* **1983**, 5425.

(9) (a) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. For other applications of selenoxide elimination to the synthesis of cyclohexadienones, see: (b) Caine, D.; Frobese, A. S. *Tetrahedron Lett.* **1977**, 3107. (c) Barton, D. H. R.; Lester, D. J.; Ley, S. V. *J. Chem. Soc., Chem. Commun.* **1978**, *130*.

(10) The ester analogous to **12** but having a more electron-withdrawing diphenyl-*tert*-butylsilyl group in place of the allyl unit could be cleanly hydrolyzed to acid **i**.

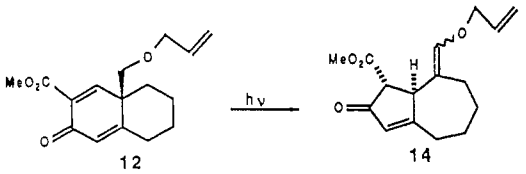


i

Table I

entry	solvent	conc, M	yield, % 17	18	19
1	anhydrous toluene	0.015	33	19	<5
2	anhydrous dioxane	0.0045	42	20	<5
3	dioxane–H_2O (95:5)	0.0045	28	35	25
4	dioxane–H_2O (85:15)	0.0045	21	32	21
5	dioxane–H_2O (95:5)	0.022	14	38	25
6	AcOH–H_2O (55:45)	0.0045	23	45	5
7	AcOH–H_2O (55:45)	0.015	26	48	6
8	anhydrous pyridine	0.0045	30	<5	<5
9	pyridine–H_2O (95:5)	0.0045	41	8	21
10	2,6-lutidine–H_2O (95:5)	0.0045	36	11	22

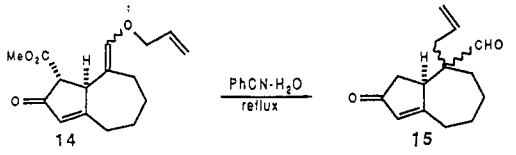
Being unable to prepare the desired acid, we undertook a study of the photochemical behavior of ester **12**. Irradiation of this material in acidic media (e.g. aqueous acetic acid) was precluded by its rapid aromatization to the methyl ester of **13** under these conditions. However, we were pleased to find that irradiation of **12** in anhydrous toluene (450-W medium-pressure Hanovia lamp, Pyrex filter) led to the enol ethers **14** in excellent yield as an inseparable mixture of *E* and *Z* isomers (eq 1).[11]



12 14 81% (1)

The ratio of double bond isomers was ~2.1; however, we have been unable to determine reliably which predominated. The α-stereochemistry of the carbomethoxy group was indicated by the small (J = 3 Hz) coupling constants exhibited by the β-keto ester protons of both isomers.[3]

Conversion of **14** to **15** (epimer ratio 2:1) was accomplished by refluxing the enol ethers in 1% aqueous benzonitrile (1 h, Ar) (eq 2). As we were not able to separate

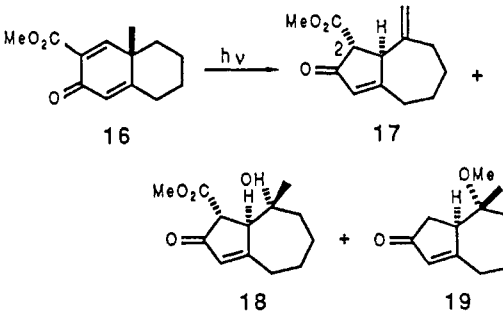


14 15 73% (2)

the *E* and *Z* isomers of **14**, we can draw no conclusions regarding the stereospecificity of the Claisen rearrangement. The fortuitous decarbomethoxylation observed under these conditions is perhaps not surprising. Krapcho and others have observed that hydrolysis and decarboxylation of β-keto esters occurs readily in moist refluxing dimethyl sulfoxide.[12] The considerable polarity and high boiling point of benzonitrile (190 °C) suggest that the present reaction may be similar in nature.

What is quite surprising is that photorearrangement of **12** in toluene gave rise to **14** at all. As has been mentioned, irradiation of cross-conjugated cyclohexadienones under neutral conditions typically results in the formation of cyclopropyl ketones (**8**) or of phenols which arise from these as secondary photoproducts.[4] No more than trace amounts of either of these materials were produced by irradiation of **12**.

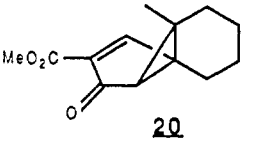
In an effort to gain some insight into the mechanism of this reaction, the known ester **16** was prepared from the corresponding enone using the three-step process employed to generate **12** and irradiated under a variety of conditions. Three major products were obtained (eq 3).



16 17 18 19 (3)

Our results are summarized in Table I. The structure of **17** could be inferred from the similarity of its ^1H and ^{13}C NMR spectra to that of **5**. Again, the stereochemistry of the C-2 carbomethoxy group was indicated by the 3-Hz coupling exhibited by the β-keto ester proton (δ 3.19). This proton readily exchanged with deuterium. Treatment of **17** with acid or base under conditions which led to deuterium incorporation at C-2 produced none of its β-carbomethoxy epimer, indicating that **17** is the thermodynamically favored stereoisomer. Compounds **18** and **19** are both known[3b] and their identities were established by comparison with authentic samples prepared according to the procedures of Caine.

As indicated in Table I, irradiation of **16** in neutral solvents gives rise primarily to hydroazulenone products whose formation would not appear to involve cyclopropyl ketone **20** as an intermediate. From all of these reactions

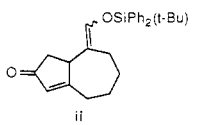


20

a phenolic product, methyl 2-hydroxy-4-methyl-5,6,7,8-tetrahydronaphthalene-1-carboxylate, could be isolated, but only in trace (<5%) amounts. It presumably arises as a secondary photoproduct of **20**. The structure of this phenol follows from mechanistic considerations and from its ^1H NMR spectrum, which shows signals for the aromatic (δ 6.69) and methyl (δ 2.19, 3.93) protons whose chemical shifts are in good agreement with those reported for similarly substituted phenolic systems.[13] Irradiation of **16** was also performed by using 2537-Å light (low-pressure mercury lamp) in dioxane–water (95:5).[14] Again **17**, **18**, and **19** were the only characterizable products obtained. They were isolated in poor overall yield owing to their photolability under these conditions.

Control experiments were performed to determine whether any of **17**, **18**, or **19** might themselves be secondary photoproducts arising from one of the others during the

(11) The acid i (footnote 10) gave rise to a 1:1 mixture of enol ethers ii upon photolysis in dry dioxane (75% yield).



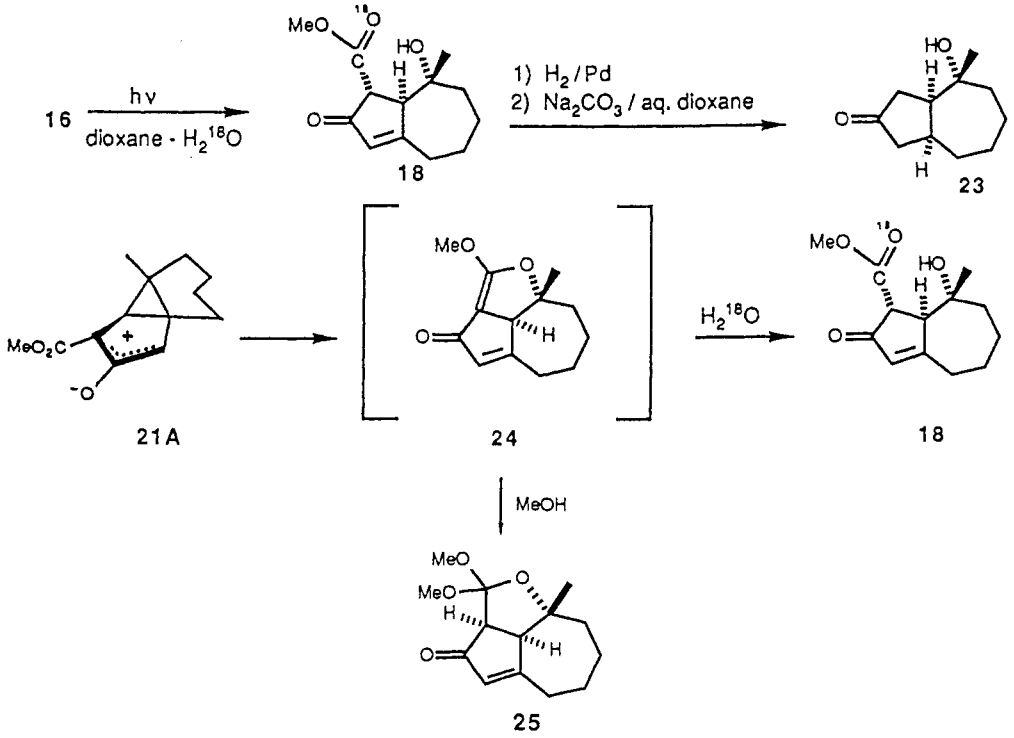
ii

(12) Krapcho, A. P.; Weimaster, J. F.; Eldridge, J. M.; Jahngen, E. G. E., Jr.; Lovey, A. J.; Stephens, W. P. *J. Org. Chem.* **1978**, *43*, 138 and references cited therein.

(13) Chan, T. H.; Brownbridge, P. *J. Am. Chem. Soc.* **1980**, *102*, 3534.

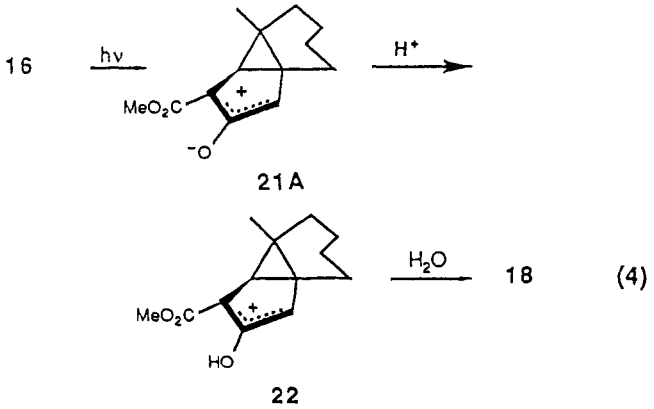
(14) Employing such conditions it is often possible to isolate cyclopropyl ketones that are unstable to longer wavelength ultraviolet light (see ref 4a).

Scheme IV



course of the reaction. Such was not the case. Both **17** and **19** proved quite stable to irradiation (450-W medium-pressure Hanovia lamp, Pyrex filter) in all the solvents which had been employed. Alcohol **18** underwent some decomposition on prolonged irradiation but produced no **17** or **19**.

Alcohol **18**, the photoproduct expected under acidic conditions, is indeed formed in aqueous acetic acid[3b] (entries 6, 7) as it is to a lesser extent in wet dioxane (entries 3–5). Its production under these conditions was initially assumed to involve the intermediacy of protonated species **22** (eq 4).



(4)

Such a mechanism cannot, however, account for the formation of **18** under anhydrous conditions (entries 1, 2). When **16** was irradiated (substrate concentration 0.045 M) in 95:5 dioxane–$H_2{}^{18}O$ **18** was obtained in 45% yield. Field ionization mass spectral analysis indicated incorporation of one ^{18}O atom per molecule of **18**. However, a fragment ion was observed in its electron impact mass spectrum which corresponded to the loss of $H_2{}^{16}O$ rather than to the loss of $H_2{}^{18}O$. Hydrogenation[3b] of labeled **18** (H_2/Pd–C/EtOH) led to its dihydro derivative, which retained the ^{18}O label. The mass spectrum of the dihydro derivative also exhibited a fragment ion corresponding to the loss of $H_2{}^{16}O$. Decarbomethoxylation[3b] of the saturated β-keto ester (sodium carbonate in aqueous dioxane) gave rise to **23**, which was found by field ionization mass spectrometry to be labeled only to the extent of about 10% (Scheme IV). The ^{13}C NMR spectrum of labeled **18** showed a 0.037 ppm upfield isotope shift[15] for the ester carbonyl carbon (δ 170.1). The other carbon resonances were unaffected.

This result suggests that in the presence of relatively small amounts of water (and, presumably, under anhydrous conditions also) the major pathway leading to **18** involves attack by the carbomethoxy group of **21A** on the electron-deficient C-9 position to generate **24**, whose subsequent hydrolysis affords the alcohol. When excess methanol was added to the mixture obtained upon irradiation of **16** (0.009 M) in anhydrous dioxane immediately after irradiation had been stopped there was isolated, in addition to **17** (29%) and minor byproducts, a new product (~50%) whose formation was not observed when such reaction mixtures were quenched with water or directly chromatographed after evaporation. The spectral data suggest that this product is the ortho ester **25**, apparently the product of trapping of **24** with methanol. In particular, its IR spectrum fails to reveal the presence of an ester function and its ^1H NMR spectrum shows it to contain two OMe units (δ 3.22, 3.32). The fact that its two five-membered rings are cis-fused is indicated by the 8-Hz coupling constants[3b] exhibited by H-1 and H-2. Compound **25** is relatively unstable, undergoing conversion to **18** in the presence of moisture.

It was also possible to obtain direct spectroscopic evidence for the existence of **24**. A solution of **16** in benzene-d_6 (0.1 M) was irradiated (25 min) in a sealed NMR tube. The ^1H NMR spectrum of the product showed, in addition to peaks derived from **17**, a vinylic resonance at δ 5.55, a methoxy singlet (δ 4.20), a methyl singlet (δ 0.79), and a singlet at δ 4.85, probably corresponding to H-1. Compounds **24** and **17** were found to be formed in roughly

(15) Vederas, J. C. *Can. J. Chem.* **1982**, *60*, 1637. The isotope shift was determined on a GN 500 spectrometer using a mixture of labeled and unlabeled **18**.

Scheme V

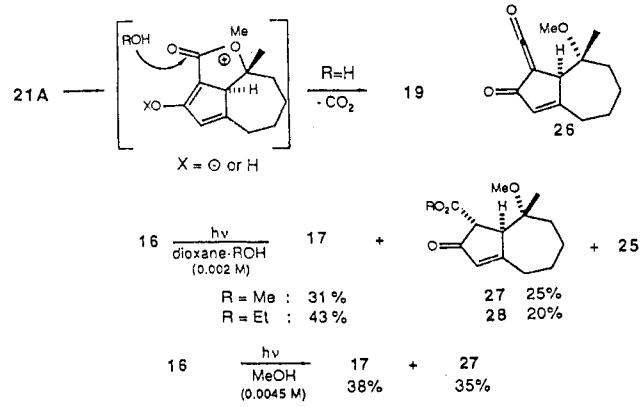


Table II

conditions	substrate conc, M	yield, % 17	25	27
photolysis in dioxane and then methanol quench	0.0045	44	47	0
	0.022	42	38	0
photolysis in dioxane–methanol (95:5)	0.0045	30	25	30
	0.022	21	46	25

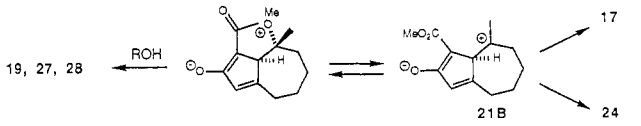
equal amounts under these conditions. Addition of methanol to the contents of the NMR tube followed by solvent removal gave **17** and **25** in a ratio of ~1:1.

The formation of **19** would appear to involve trapping of an oxonium ion intermediate by water (Scheme V) as is indicated by the following series of results. Irradiation of **16** in methanol or dioxane–methanol (95:5) produced, along with **17**, the ester **27**. Irradiation in dioxane–ethanol (95:5), however, led to the ethyl ester **28**. The ethyl ether, which would be the expected product of trapping of **22** by ethanol, was not formed in significant amount. When **16** was irradiated in dioxane–D_3COD (95:5) the **27** obtained was found to be extensively deuteriated at the ester methyl (δ 3.76), whereas the intensity of the ether methyl signal (δ 3.15) was undiminished. These results imply clearly that transfer of the methoxy group takes place in an intramolecular fashion. Compound **25** was also formed when **16** was photolyzed in dioxane–methanol, as would be expected. Although the yield of **25** could be estimated from the NMR spectrum of the crude reaction mixtures (vide infra), no attempt was made to isolate this product owing to its instability.

While allowing us to delineate the overall sequence of events leading to the formation of **19**, **27**, and **28**, the foregoing results do not exclude the possible intermediacy of ketene **26** in these transformations. That is, they do not tell us whether cleavage of the original CO–OMe bond occurs along with formation of the new CO–OR bond or, instead, precedes it. Accordingly, a series of experiments were performed in which **16** was either irradiated (0.5 h) in dry dioxane then quenched with methanol or simply irradiated in dioxane–methanol (95:5). The reaction mixtures were evaporated and the yields of **17**, **25**, and **27** determined (Table II) by ^1H NMR (integrating well-resolved signals by using 2,4,5-trichloronitrobenzene as the internal standard). Determination of yields in this manner allowed us to overcome the problems posed by the lability of **25** to silica gel chromatography.

As can be deduced from the above results, these reactions proceeded cleanly, affording **17**, **25**, and **27** as the only major products. Since **27** was not obtained when the crude photorearrangement products were quenched with methanol, ketene **26** either does not form at all in anhydrous dioxane or it does but is unstable. However, the combined yields of **17** and **25** obtained under these conditions are quite high, indicating that material is not being lost to the decomposition of any labile intermediate. To the extent that it is difficult to write appealing mechanisms for the obtention of either **17** or **25** from **26** it is more reasonable to assume the intermediacy of a reversibly formed oxonium ion (Scheme V) in the generation of ethers such as **27** and **19**. Alternatively, one could argue that the oxonium ion or ketene **26** only forms in the presence of methanol, water, or a similar proton source, although it is not obvious why this should be the case. If the oxonium ion forms in anhydrous dioxane, where it cannot be intercepted by nucleophiles, it is more likely to equilibrate with the less strained bicyclic zwitterion **21B** than with **21A**. Since **17** and **24** (the precursor of **25**) are both produced in high yield under these conditions, the implication would then be that **21B** is capable of giving rise to these two products (Scheme VI). Indeed, no evidence excludes the possibility that zwitterion **21A**, perhaps as a consequence of destabilization of the oxyallyl cation moiety by the electron-withdrawing ester group, opens rapidly to **21B** and that both **17** and **24** originate solely from this species.[16,17]

Scheme VI

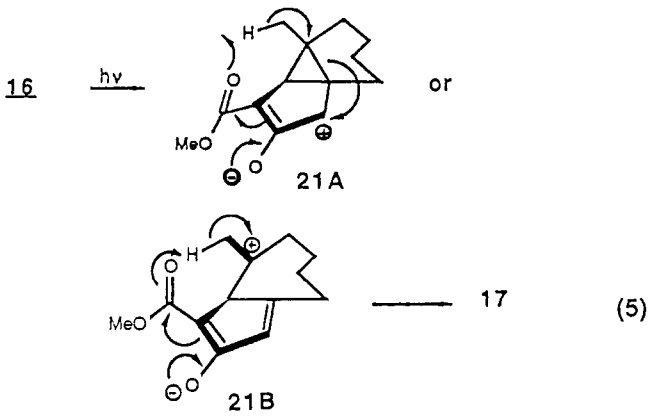


The formation of **17** by the intramolecular deprotonation mechanism illustrated (eq 5) is consistent with the available data. It is tempting to invoke participation by the ester group in the deprotonation since this allows us to rationalize the exclusive formation of the *exocyclic* olefin in these reactions. It also explains the fact that such olefins are only observed as the photoproducts of dienones bearing ester or carboxy functions at C-2. Those lacking ester or carboxy substituents at this position typically give products of S_N2 attack at C-9 when irradiated in acidic solvents, but **16** gives considerable amounts of **17** even in aqueous acetic acid. Moreover, irradiations performed in basic solvents (entries 8–10) did not result in significantly higher yields of **17** than were obtained in toluene or dioxane. Examination of models indicates that proton abstraction by the ester carbonyl is a stereoelectronically reasonable process in the case of **21B** and probably reasonable also in the case of **21A** if a rather late transition state[3a] is assumed (eq 5).

Regardless of the base involved, an obvious question concerns the identity of the species which undergoes deprotonation to give **17**. The evidence strongly suggests that **21B** or the Zimmerman–Schuster zwitterion **21A** are sources of **17**. The formation of **17** was greatest in anhydrous solvents (entries 1, 2). If the oxyallyl cation **22** were an obligatory intermediate on route to **17** this would not have been the case. Under conditions expected to favor protonation of **21A** (entries 6, 7) formation of **17** was diminished but not eliminated entirely. This may, conceivably, be due to the rate of formation of **17** being competitive with that of protonation of **21A**. However, Caine's observation[3] that **4** gives rise to a similar olefin (**5**) casts

(16) The stereoselective generation of **18** as the indicated carbinol epimer does not rule out this possibility since **18** evidently arises via an intramolecular process capable of affording only this stereoisomer.

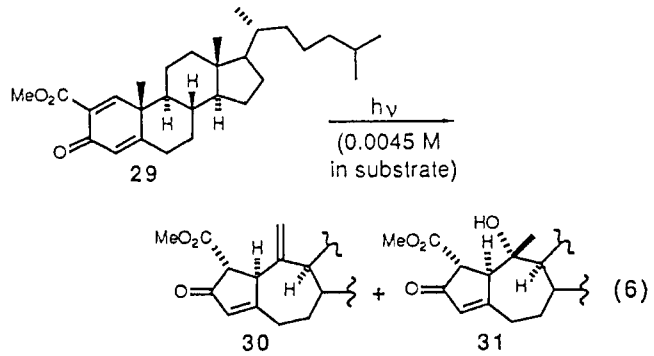
(17) In certain cases (see Table I) the photolysis of **16** under anhydrous conditions did lead to the formation of small amounts of **19**. Whether these results reflect the operation of a minor pathway, perhaps involving **26** as an intermediate, or are due instead to the presence of adventitious water is not clear at this time.



(5)

doubt on this interpretation. Internal protonation of the Zimmerman–Schuster zwitterion derived from **4** should be essentially simultaneous with its formation,[18] and yet **5** is obtained from it in high yield in the absence of external nucleophiles. Taken together these facts suggest that olefin formation can occur both from the zwitterions **21A** or **21B** as well as from the corresponding oxyallyl cations.[19,20]

We also examined briefly the photochemical rearrangement of the steroidal cyclohexadienone ester **29** which was prepared from Δ^4-cholestenone by using the previously described carbomethoxylation–selenation–oxidation sequence (overall yield 83%) (eq 6). Production of phenolic

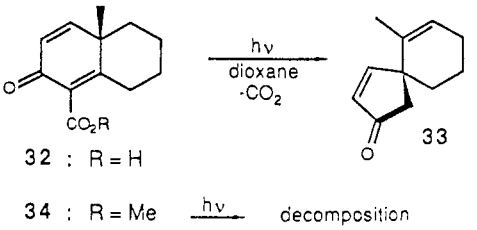


(6)

Anhydrous Toluene	14%	30%
Dioxane - H_2O (95:5)	8%	50%
Pyridine - H_2O (95:5)	15%	29%

materials (three isomers, combined yields ca. 10%) took place to a slightly greater extent with **29** than with **12** or **16**. The steroidal system also exhibited a decreased propensity for exocyclic olefin formation. Moreover, no ether corresponding to **19** was detected among its photoproducts.

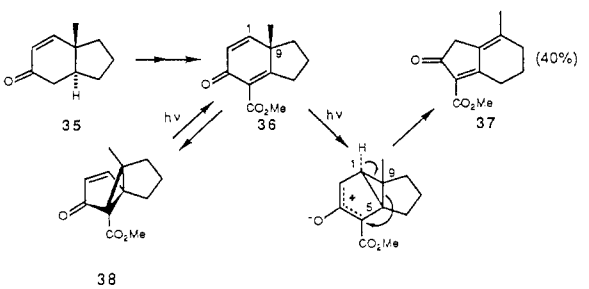
In his first report[3a] dealing with the photochemistry of acid **4** Caine also suggested that formation of **5** involved intramolecular proton abstraction (in this case by the carboxylate moiety). This view was later rejected owing to the exclusive formation of the endocyclic olefin **33** from the 4-carboxy dienone **32** (eq 7).[3b]



(7)

In order to shed more light on this question as well as to assess further the generality of olefin formation from cyclohexadienone esters, **34**[3b] was submitted to irradiation in neutral media. Caine[3b] has already observed that **34** does not rearrange to hydroazulenic or spirocyclic products in aqueous acetic acid. It was suggested that this might be the result of photochemically promoted deconjugation of the 4,10-double bond competing with the normal β,β'-bonding process. Our irradiation of **34** under neutral conditions also led to no identifiable products. We then prepared the 6/5-fused system **36** from the *trans*-hydindenone **35**[21] using the same sequence of reactions employed for the synthesis of **12** (73% overall yield). We reasoned that deconjugation of **36** might prove less tolerable owing to the preference on the part of double bonds to locate themselves endocyclic with respect to six-membered rings and exocyclic with respect to five-membered rings.[22,23] If so, our chances of obtaining spirocyclic photoproducts from it would be improved.

Indeed, a photoproduct could be isolated in fair yield from **36** upon irradiation in toluene (eq 8) however it proved to be the 5/6-fused dienone **37**, which results from an abnormal photorearrangement of a type well-precedented for 6/5-fused cyclohexadienones[24,25] such as **36** and also for their ring-B norsteroid counterparts.[26] These



(8)

rearrangements appear to proceed through the usual Zimmerman–Schuster zwitterions but formally involve loss of a proton from the cyclopropyl ring as indicated. When the irradiation of **36** was interrupted in midcourse a different photoproduct could be isolated. It was found to be the cyclopropyl ketone **38**. Irradiation of **38** gave rise to both **36** and **37**. The photochemically promoted reversion of

(18) Ultraviolet spectroscopy indicates the dienone oxygen of **4** to be strongly hydrogen bonded (Dreiding, A. S.; Tomasewski, A. J. *J. Org. Chem.* **1954**, *19*, 241).

(19) The formation of **17**, **18**, and **19** was also studied as a function of time. Photolyses were performed in the usual manner and aliquots were withdrawn at 5-min intervals, evaporated, and examined by ^{1}H NMR. Each of **17**, **18**, and **19** were produced at a nearly constant rate.

(20) There is one effect for which we presently have no convincing explanation. It involves the relationship between substrate concentration and the relative amounts of **17** and **18** formed in aqueous dioxane and the relative amounts of **17** and **25** formed in methanolic dioxane. Photolyses performed under dilute conditions (0.002–0.006 M in substrate) resulted in consistently higher yields of **17** than did those performed at higher concentrations (e.g., entry 5). This concentration dependence was not observed in aqueous acetic acid where relatively more **18** than **17** was always produced (entries 6, 7).

(21) Stork, G.; Shiner, C. S.; Winkler, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 310.

(22) (a) Brown, H. C.; Brewster, J. H.; Shechter, H. *J. Am. Chem. Soc.* **1954**, *76*, 467. (b) Gorodetsky, M.; Luz, Z.; Mazur, Y. *Ibid.* **1967**, *89*, 1183.

(23) For an earlier commentary on this phenomenon, see: Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510.

(24) Caine, D.; Alejande, A. M.; Ming, K.; Powers, W. J., III. *J. Org. Chem.* **1972**, *37*, 706.

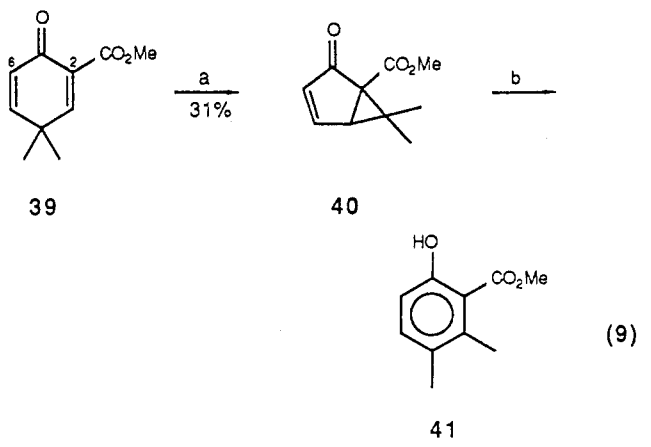
(25) Caine, D.; Gupton, J. T., III; Ming, K.; Powers, W. J., III. *J. Chem. Soc., Chem. Commun.* **1973**, 469.

(26) Bozzato, G.; Throndsen, H. P.; Schaffner, K.; Jeger, O. *J. Am. Chem. Soc.* **1964**, *86*, 2073.

cyclopropyl ketones such as **38** to their corresponding 6/5-fused dienone precursors is precedented and its mechanism has been explained.[24,27]

While doing little to clarify the nature of the proton abstraction step leading to **17** and related olefins, this result is not without interest. The central question raised by the photochemical rearrangements of **12**, **16**, and **29** under neutral conditions is this: why are hydroazulenic materials, whose formation would normally be expected only under acidic conditions, obtained instead of cyclopropyl ketones (e.g. **20**) or their phenolic degradation products? Intramolecular protonation of the Zimmerman–Schuster zwitterion, which may well take place with the acid **4**, cannot be invoked to explain the atypical photorearrangements of the esters **12**, **16**, and **29**. Nor can it be responsible for the fact that several dienones analogous to **16** but having formyl groups at C-2 also do not undergo normal type-A photorearrangements when irradiated under neutral conditions.[3b,28] The divergent behavior of compound **36** suggests that the location of the carbomethoxy group in relation to the migrating bond influences the facility of the [1,4] sigmatropic shift which must lead to the cyclopropyl ketone. Thus, when the ester substituent occupies the position to which the new bond is formed, a type-A photorearrangement is observed. When the ester substituent occupies the alternative position, as is the case with compound **16**, the [1,4] shift is rendered less favorable and other processes supervene in its absence. Electron-withdrawing[29,30] and electron-donating[31-33] substituents present on the dienone chromophore have been shown to significantly effect both the rate and the regiochemical outcome of type-A photorearrangements of monocyclic cyclohexadienones which, unlike the bicyclic systems **16** and **36** have a choice between affording either of two possible cyclopropyl ketone products. In light of the forgoing discussion, the monocyclic system **39**[34] would be expected to give cyclopropyl ketone **40** upon irradiation, and we have found that this is, in fact, the case (eq 9).

When **39** is irradiated briefly with a low-pressure mercury lamp[14] a normal type-A photorearrangement takes place, giving **40**. Upon further irradiation at 2537 Å this compound, not unexpectedly, rearranges to phenol **41**. This phenol is the sole characterizable product obtained (43%) when a toluene solution of **39** (0.007 M) is irradiated with Pyrex-filtered light. Irradiation of **39** gave rise to no products analogous to **17**, **18**, or **19**. The exclusive formation of ketone **40** as opposed to its isomer which would have resulted from bond migration to C-6 is easily understandable. To the extent that negative charge or radical character is distributed at C-2 during the observed sigmatropic shift, it enjoys the stabilization provided by the adjacent carbomethoxy group. The transition state for the alternative [1,4] shift is not stabilized in this manner. Evidently, it is only in those cases where the more favorable [1,4] shift is precluded by geometrical constraints that processes such as those leading to **17**, **18**, and **19** become operative.



(9)

(a) 2537-Å light, dioxane; (b) extended radiation.

Experimental Section

General Procedures. Analytical TLC was performed on Merck 0.25-mm glass silica gel plates: visualization of developed plates was by fluorescence quenching and staining with a solution of *p*-anisaldehyde–AcOH–H_2SO_4–95% aqueous EtOH (0.9:0.37:1.23:33). Preparative TLC was performed with Merck Kieselgel 60 (230–400 mesh). Column chromatography utilized Brinkmann silica gel (50–200 μm). THF, Et_2O, and benzene were distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2. Toluene was distilled from sodium. Dioxane was distilled from lithium aluminum hydride. Moisture-sensitive reactions were performed in oven-dried (135 °C) glassware. Air-sensitive reactions were performed under argon. IR spectra were obtained on an IBM/32 FTIR spectrophotometer as films on NaCl disks or in $CHCl_3$ solution. ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 (300 MHz for proton, 75.4 MHz for carbon) spectrometer in $CDCl_3$ with $CHCl_3$ (δ 7.26) as internal standard. Low-resolution mass spectra were obtained on a Finnigan-MAT CH-5 spectrometer using an ionization voltage of 70 eV. High-resolution and field ionization mass spectra were obtained on a Finnigan-MAT 731 spectrometer. Chemical ionization mass spectra were obtained with a VG-705E spectrometer.

3-Keto-9-[(allyloxy)methyl]-Δ⁴-octahydronaphthalene. Alcohol **10** (6.38 g, 28.5 mmol) in 50 mL of THF was added to a stirred suspension of KH (1.78 g, 44.5 mmol) in 50 mL of THF at 0 °C over a period of 10 min. Once hydrogen evolution had ceased allyl bromide (3.2 mL, 37 mmol) was introduced and the reaction allowed to continue at 0 °C for 2 h. After careful addition of MeOH to destroy the remaining KH the reaction mixture was poured into water and extracted with several portions of ether. Drying of the organic phases over $MgSO_4$ and solvent removal gave the crude (allyloxy)methyl ketal, which was hydrolyzed without further purification.

The crude ketal was dissolved in 70 mL of MeOH and 40 mL of 10% aqueous hydrochloric acid was added. The solution was refluxed 1 h and then cooled. Neutralization with saturated aqueous $NaHCO_3$ followed by extraction with ether, drying of the extract over $MgSO_4$, evaporation under reduced pressure, and Kugelrohr distillation [120 °C (1 mm)] gave the title compound (5.87 g, 94% for two steps): IR (neat) 2930, 2861, 1665, 1616 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.40 (m, 12 H), 2.60 (m, 2 H), 3.53 (s, 2 H), 3.98 (d, J = 6 Hz, 2 H), 5.23 (m, 2 H), 5.85 (s, 1 H), 5.86 (m, 1 H); HRMS calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1465.

2-Carbomethoxy-3-keto-9-[(allyloxy)methyl]-Δ¹,⁴-hexahydronaphthalene (12). A solution of *n*-butyllithium (1.5 M) in hexane (550 μL, 0.825 mmol) was added to diisopropylamine (120 μL, 0.86 mmol) in 1.5 mL of THF at −20 °C. The mixture was stirred at this temperature for 30 min and then cooled to −78 °C. A solution of 3-keto-9-[(allyloxy)methyl]-Δ⁴-octahydronaphthalene (154 mg, 0.7 mmol) in 1 mL of THF was added, and the mixture was allowed to warm to 0 °C and stirred 1 h. The reaction mixture was cooled to −78 °C and treated with HMPA

(27) Such reversions have not been observed in the case of 6/6-fused systems. That the do not occur with the 2-carbomethoxy-substituted dienones we have studied is indicated by the fact of our obtaining single regioisomers (**30** and **31**) from the ring-B unsymmetrically substituted dienone **29** (see ref 24).

(28) Altenburger, v. E.; Wehrli, H.; Schaffner, K. *Helv. Chim. Acta* **1963**, *46*, 2753.

(29) Stille, J. K.; Rettig, T. A.; Kuemmerle, E. W., Jr. *J. Org. Chem.* **1976**, *41*, 2950.

(30) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4864.

(31) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4876.

(32) Matoba, K.; Karibe, N.; Yamazaki, T. *Chem. Pharm. Bull.* **1982**, *30*, 3906.

(33) Matoba, K.; Kawagoshi, F.; Tanabe, M.; Yamazaki, T. *Chem. Pharm. Bull.* **1985**, *33*, 3709.

(34) Liu, H. J.; Browne, E. N. C. *Can. J. Chem.* **1981**, *59*, 601.

(76 μL, 0.42 mmol) followed by methyl cyanoformate (100 μL, 1.17 mmol). The mixture was stirred for 30 min at −78 °C, allowed to warm to room temperature, and then partitioned between ether and water. The ether layer was washed with water and brine, and then the solvent was removed under reduced pressure. The crude β-keto ester was purified by PTLC (30% EtOAc in hexane) to afford **11** (115 mg, 60%); ^{1}H NMR δ 1.20–2.40 (m, 10 H), 3.55 (m, 2 H), 3.80 (s, 3 H), 3.90 (d, J = 6 Hz, 2 H), 5.20 (m, 2 H), 5.80 (m, 2 H).

A solution of **11** (113 mg, 0.40 mmol) in 1 mL of THF was added to a suspension of KH (21 mg, 0.53 mmol) in 1 mL of THF at 0 °C. (It was occasionally necessary to add a drop of MeOH to the mixture of the β-keto ester and KH to initiate reaction.) After hydrogen evolution had ceased (about 10 min) a solution of benzeneselenenyl chloride (92 mg, 0.48 mmol) in 1.5 mL of THF was added. The reaction was diluted with water and extracted with ether after being stirred 10 min. The ether extracts were evaporated to yield the crude selenide which was then dissolved in 3 mL of CH_2Cl_2. Water (1 mL) and 30% aqueous hydrogen peroxide (0.2 mL, 1.76 mmol) were added, and the resulting two-phase mixture was vigorously stirred for 7 min, whereupon it was diluted with CH_2Cl_2 and the organic layer washed several times with aqueous $NaHCO_3$. Solvent removal and PTLC (50% EtOAc in hexane) gave **12** (82 mg, 73%): IR (neat) 3015, 2950, 2870, 1735, 1660, 1630 cm^{-1}; ^{1}H NMR δ 1.20–2.40 (m, 8 H), 3.52 (d, J = 9 Hz, 1 H), 3.68 (d, J = 9 Hz, 1 H), 3.81 (s, 3 H), 3.89 (d, J = 6 Hz, 2 H), 5.21 (m, 2 H), 5.80 (m, 1 H), 6.19 (s, 1 H), 7.55 (s, 1 H); HRMS calcd for $C_{16}H_{20}O_4$ 276.1361, found 276.1360.

2-Carbomethoxy-3-keto-9-methyl-Δ^{1,4}-hexahydronaphthalene (16). This ester was prepared from 3-keto-9-methyl-Δ^4-octahydronaphthalene by the same procedures utilized for the synthesis of **12**. In this case the intermediate β-keto ester required no chromatographic purification. Ester **16** was purified by crystalization from hexane, and its spectral data agreed with those reported in the literature.[3] The yield was 63% for three steps.

2-Carbomethoxy-Δ^{1,4}-cholestadien-3-one (29). This compound was prepared from Δ^4-cholestenone as described for **12**. The product was purified by flash chromatography over silica gel (15% EtOAc in hexane). The yield for three steps was 83%; oil; IR (neat) 2930, 1741, 1660, 1636, 1271 cm^{-1}; ^{1}H NMR δ 0.69 (s, 3 H), 1.24 (s, 3 H), 0.9–2.2 (m, 33 H), 3.80 (s, 3 H), 6.05 (s, 1 H), 7.67 (s, 1 H); HRMS (chemical ionization) calcd for $C_{29}H_{44}O_3$ + H 441.3367, found 441.3360.

4-Carbomethoxy-7a-methyl-5(7a*H*)-indanone (36). This compound was prepared, in the previously described manner, from *trans*-hydrindanone **35**.[21] The product was purified by flash chromatography over silica gel (eluting with a 0–20% gradient of EtOAc in hexane) and obtained in 73% yield for three steps: IR (neat) 2963, 1734, 1659, 1607 cm^{-1}; ^{1}H NMR δ 1.25 (s, 3 H), 1.60–3.0 (m, 6 H), 3.81 (s, 3 H), 6.19 (d, J = 12 Hz, 1 H), 7.01 (d, J = 12 Hz, 1 H); HRMS calcd for $C_{12}H_{14}O_3$ 206.0942, found 206.0936.

General Irradiation Procedure. (a) Small Scale: Illustrated for Irradiation of 12. A solution of **12** (37 mg, 0.13 mmol) in 7 mL of anhydrous toluene (0.02 M) in a 20 cm × 1 cm quartz test tube was sealed with a septum and placed in contact with a water-cooled immersion well housing a 450-W Hanovia medium-pressure mercury vapor lamp shielded with a Pyrex filter. The solution was bubbled with nitrogen for 10 min by means of a needle inserted through the septum and reaching to the bottom of the tube. (A separate needle was introduced to permit escape of nitrogen.) A stream of compressed air was blown over the tube to dissipate heat generated by the lamp, and the entire assembly was surrounded by aluminum foil. The lamp was turned on, and the irradiation was allowed to proceed for 40 min while nitrogen was gently bubbled through the solution. At the end of this time the solution was evaporated under reduced pressure and the products **14** isolated by PTLC on silica gel (35% EtOAc in hexane). The yield of **14** was 30 mg (81%); IR ($CHCl_3$) 2940, 1735, 1700, 1620 cm^{-1}; ^{1}H NMR δ 1.2–3.0 (m, 8 H), 3.06 (d, J = 3 Hz) and 3.15 (d, J = 3 Hz) (together 1 H, ratio ca. 2:1), 3.71 (s) and 3.76 (s) (together 3 H, ratio ca. 2:1), 4.18 (m), 4.25 (d, J = 6 Hz), and 4.41 (together 3 H, allylic methylenes and doubly allylic methine), 5.22 (m, 2 H), 5.85 (m, 1 H), 5.92 (s, 1 H), 6.03 (s), and 6.05 (s) (together 1 H, vinyl ether protons); ^{13}C NMR δ 24.2, 29.1, 29.5, 29.6, 31.1, 31.9, 32.0, 32.8, 48.1, 51.3, 52.3, 52.4, 60.3 and 60.6, 72.6 and 72.7, 115.1, 116.1, 117.2, 117.4, 128.1 and 128.6, 133.5 and 133.6, 143.7 and 143.8, 169.3 and 169.9, 185.3 and 185.4, 201.4 and 202.6; HRMS calcd for $C_{16}H_{20}O_4$ 276.1361, found 276.1360.

Claisen Rearrangement–Decarbomethoxylation of 14. A solution of **14** (20 mg, 0.081 mmol) in 1 mL of 1% aqueous benzonitrile was refluxed for 45 min (argon atmosphere) and then evaporated under reduced pressure. The residue was purified by PTLC on silica gel (35% EtOAc in hexane) to give 13 mg (73%) of **15** as a ca. 2:1 mixture of stereoisomers: oil; IR (neat) 1726, 1694 cm^{-1}; ^{1}H NMR δ 1.5–3.4 (m, 13 H), 5.19 (m, 2 H), 5.75 (m, 1 H), 5.97 and 6.03 (both s, ratio 1:2, together 1 H), 9.53 and 9.54 (both s, ratio 1:2, together 1 H); HRMS calcd for $C_{14}H_{18}O_2$ 218.1306, found 218.1306.

Dienoic Ester 37. A solution of **36** (30 mg, 0.14 mmol) in 6 mL of toluene (0.024 M) was irradiated in the manner described for **12**. The product was isolated by PTLC on silica gel (50% EtOAc in hexane). The yield of **37** was 12 mg (40%): IR ($CHCl_3$) 3010, 2910, 1730, 1700 cm^{-1}; ^{1}H NMR δ 1.25 (m, 2 H), 1.85 (t, J = 6 Hz, 2 H), 1.90 (s, 3 H), 2.28 (br t, J = 6 Hz, 2 H), 3.00 (br s, 2 H), 3.83 (s, 3 H); ^{13}C NMR δ 21.7, 26.0, 29.7, 31.1, 38.3, 51.6, 125.7, 129.7, 145.0, 164.1, 178.0, 199.5; HRMS calcd for $C_{12}H_{14}O_3$ 206.0942, found 206.0941.

Cyclopropyl Ketone 38. A solution of **36** (27 mg, 0.12 mmol) in 5 mL of toluene was irradiated for 25 min, then evaporated, and chromatographed in the manner described above to afford (in order of decreasing R_f on silica gel) **38** (3 mg, 11%) [IR ($CHCl_3$) 2929, 1732, 1695 cm^{-1}; ^{1}H NMR δ 1.22 (s, 3 H), 1.8–2.4 (m, 6 H) 3.74 (s, 3 H), 5.90 (d, J = 6 Hz, 1 H), 7.35 (d, J = 6 Hz, 1 H); HRMS calcd for $C_{12}H_{14}O_3$ 206.0942, found 206.0941], recovered **36** (5 mg, 19%), and **37** (7 mg, 26%).

(b) Large Scale: Illustrated for Irradiation of 16 (Table I). The amount of **16** required to afford the indicated concentration was dissolved in 50 mL of the appropriate solvent in a 100-mL Pyrex flask and placed adjacent to a quartz immersion well housing a 450-W medium-pressure Hanovia lamp and the apparatus assembled as described for the small scale runs. In the case of reactions performed under aqueous conditions the solution was purged of dissolved oxygen and then irradiated for 40 min while N_2 was bubbled through the solution. In the case of reactions requiring to be performed under anhydrous conditions the solution was first bubbled briefly with dry argon and then activated 4A molecular sieves (3 g) were introduced. The flask was then sealed, and the solution was stirred for 2 h prior to irradiation. Stirring was continued during the irradiation itself. In all cases disappearance of starting material was complete. (In several of the timed runs the starting material was consumed within 20 min; however, continued irradiation did not noticably effect the product ratios.) The solvent was then evaporated under reduced pressure and the products isolated by PTLC on silica gel (35% EtOAc in hexane). In order of decreasing R_f, the products were methyl 2-hydroxy-4-methyl-5,6,7,8-tetrahydronaphthalene-1-carboxylate [IR ($CHCl_3$) 1690 cm^{-1}; ^{1}H NMR δ 1.60–1.95 (m, 4 H), 2.19 (s, 3 H), 2.55 (br t, J = 6 Hz, 2 H), 2.98 (br t, J = 6 Hz, 2 H), 3.93 (s, 3 H), 6.69 (s, 1 H), 10.88 (s, 1 H); HRMS calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1100], olefin **17** [oil; IR (neat) 2933, 2855, 1741, 1711, 1645, 1613, 1437, 1338, 1146, 903 cm^{-1}; ^{1}H NMR δ 1.20–2.80 (m, 8 H), 3.19 (d, J = 3 Hz, 1 H), 3.79 (s, 3 H), 4.07 (br s, 1 H), 4.99 (br s, 2 H), 5.93 (s, 1 H); ^{13}C NMR δ 29.7, 31.4, 32.3, 33.6, 52.6, 54.5, 60.1, 115.6, 128.1, 147.2, 169.2, 184.4, 201.1; HRMS calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1100], ether **19** [^{1}H NMR ($CDCl_3$) δ 0.93 (s, 3 H), 1.2–2.0 (m, 9 H), 2.42 (dd, J = 18, 6 Hz, 1 H), 2.53 (dd, J = 18, 3 Hz, 1 H), 3.21 (s, 3 H), 5.93 (s, 1 H); ^{13}C NMR δ 18.6, 24.9, 25.3, 32.7, 38.5, 39.3, 48.8, 51.3, 78.0, 131.7, 182.7, 208.6], alcohol **18** [^{1}H NMR ($CDCl_3$) δ 1.03 (s, 3 H), 1.2–3.1 (m, 8 H), 3.60 (d, J = 3 Hz, 1 H), 3.65 (br s, 1 H), 3.77 (s, 3 H), 5.88 (s, 1 H); ^{13}C NMR δ 21.2, 24.9, 25.8, 33.0, 46.7, 52.7, 55.6, 58.4, 74.1, 129.4, 170.1, 181.9, 200.5].

Also prepared in this manner were the following.

Ester **27**: oil; IR (neat) 2940, 2860, 1734, 1699 cm^{-1}; ^{1}H NMR δ 0.95 (s, 3 H), 1.20–3.05 (m, 9 H), 3.15 (s, 3 H), 3.55 (d, J = 6 Hz, 1 H), 3.76 (s, 3 H), 5.88 (s, 1 H); HRMS calcd for $C_{14}H_{20}O_4$ 252.1361, found 252.1362.

Ester **28**: oil; IR (neat) 2932, 1695, 1734 cm^{-1}; ^{1}H NMR δ 0.97 (s, 3 H), 1.30 (t, J = 7 Hz, 3 H), 1.3–3.1 (m, 8 H), 3.17 (s, 3 H), 3.54 (d, J = 4 Hz, 1 H), 3.76 (m, 3 H), 4.24 (m, 2 H), 5.88 (s, 1 H); HRMS calcd for $C_{15}H_{22}O_4$ 266.1517, found 266.1516.

From **29** were prepared in this manner (in order of decreasing R_f on silica gel) olefin **30** [oil; IR (neat) 2946, 2868, 1734, 1709, 1665, 1613 cm^{-1}; ^1H NMR δ 0.72 (s, 3 H), 0.9–3.0 (m, 33 H), 3.61 (d, J = 3 Hz, 1 H), 3.77 (s, 3 H), 3.90 (br s, 1 H), 4.81 (s, 1 H), 5.03 (s, 1 H), 5.70 (s, 1 H); HRMS calcd for $C_{29}H_{44}O_3$ 440.3289, found 440.3285] and alcohol **31** [oil; IR (neat) 3486, 2947, 2870, 1740, 1705, 1645, 1611 cm^{-1}; ^1H NMR δ 0.70 (s, 3 H), 0.96 (s, 3 H), 0.8–3.0 (m, 34 H), 3.67 (d, J = 3 Hz, 1 H), 3.70 (d, J = 3 Hz, 1 H), 3.78 (s, 3 H), 5.86 (s, 1 H); HRMS calcd for $C_{29}H_{46}O_4$ 458.3395, found 458.3391.

Ortho Ester 25. A solution of **16** (100 mg, 0.46 mmol) in 50 mL of anhydrous dioxane was purged with argon and then irradiated in the usual manner for a period of 30 min. Irradiation was discontinued, and methanol (10 mL) was introduced. The mixture was allowed to stand in the dark for 10 min. Evaporation gave a crude product, which was purified by PTLC on silica gel (40% EtOAc in hexane) to give (in order of decreasing R_f) **17** (29 mg, 29%) and **25** (59 mg) as an unstable oil: IR (neat) 2940, 1699, 1136 cm^{-1}; ^1H NMR δ 1.04 (s, 3 H), 1.4–2.95 (m, 8 H), 3.05 (d, J = 8 Hz, 1 H), 3.22 (s, 3 H), 3.32 (s, 3 H), 3.77 (d, J = 8 H, 1 H), 5.71 (br s, 1 H); HRMS calcd for $C_{14}H_{20}O_4$ 252.1361, found 252.1367.

Cyclopropyl Ketone 40 and Phenol 41. A solution of dienone **39**[34] (55 mg, 0.30 mmol) in 15 mL of dry dioxane was purged with nitrogen and placed in a Rayonet photochemical reactor equipped with low-pressure mercury lamps. After 25 min, irradiation TLC indicated the disappearance of starting material and the formation of two higher running products. The solvent was removed under reduced pressure and PTLC on silica gel (25% EtOAc in hexane) gave (in order of decreasing R_f) phenol **41** (8 mg, 15%) [IR (neat) 2955, 1663 cm^{-1}; ^1H NMR δ 2.22 (s, 3 H), 2.41 (s, 3 H), 3.96 (s, 3 H), 6.75 (d, J = 8.4 Hz, 1 H), 7.18 (d, J = 8.4 Hz, 1 H), 10.56 (br s, 1 H); HRMS calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0790] and cyclopropyl ketone **40** (17 mg, 31%) [oil; IR (neat) 2957, 1720, 1705 cm^{-1}; ^1H NMR δ 1.19 (s, 3 H), 1.36 (s, 3 H), 2.94 (dd, J = 3 Hz, 1 H), 3.77 (s, 3 H), 5.99 (d, J = 5.5 Hz, 1 H), 7.40 (dd, J = 5.5, 3 Hz, 1 H), HRMS calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0788].

Acknowledgment. We thank the Research Board of the University of Illinois, Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this work.

Registry No. (±)-**10**, 60815-97-6; (±)-**10** (allyl ether), 112042-27-0; (±)-**10** (allyl ether, ketone), 112042-28-1; (±)-**11**, 112042-31-6; (±)-**12**, 112042-32-7; (±)-**13**, 25435-10-3; (±)-(*E*)-**14**, 112042-33-8; (±)-(*Z*)-**14**, 112042-25-8; (±)-*cis*-**15**, 112042-26-9; (±)-*trans*-**15**, 112042-34-9; (±)-**16**, 112042-35-0; (±)-**17**, 112042-36-1; (±)-**18**, 112042-37-2; *carbonyl*-^{18}O-(±)-**18**, 112042-39-4; (±)-**19**, 112042-38-3; (±)-**23**, 112042-42-9; (±)-**24**, 112068-66-3; (±)-**25**, 112042-43-0; (±)-**27**, 112042-45-2; (±)-**27** (CD_3 ester), 112042-30-5; (±)-**28**, 112042-46-3; **29**, 112042-47-4; **30**, 112042-48-5; **31**, 112042-49-6; (±)-**36**, 112042-40-7; **37**, 112042-41-8; (±)-**38**, 112042-44-1; **39**, 65595-92-8; (±)-**40**, 112042-50-9; **41**, 5628-60-4; $NCCO_2Me$, 17040-15-2; (±)-3-keto-9-methyl-Δ^4-octahydronaphthalene, 40573-28-2; (±)-*trans*-2-carbomethoxy-3-keto-9-methyl-Δ^4-octahydronaphthalene, 112042-29-2; Δ^4-cholestenone, 601-57-0.

Pyridiniumcarbons: Perpyridinium Derivatives of Cyclopropene and Allyl Anion

Kenneth C. Waterman, Drew V. Speer, Andrew Streitwieser, Jr.,* Gary C. Look, Kim O. Nguyen, and Jeffrey G. Stack

Department of Chemistry, University of California, Berkeley, California 94720

Received June 16, 1987

The structure and reactivity of the first pyridiniumcarbons, compounds in which every available position is substituted by an *N*-pyridinium cation group, are discussed. Tetrakis(4-(dimethylamino)pyridinium-1-yl)-cyclopropene (**1**) and pentakis(4-(dimethylamino)pyridinium-1-yl)allylid (**2**) were prepared by reaction of tetrachlorocyclopropene with 4-(dimethylamino)pyridine, DMAP. Compound **2** was prepared from **1** by further reaction with DMAP; **1** was found to react with cyanide ion to give (*E*)-1-cyano-1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)allylid (**4**). The one isomer formed is a thermodynamic product in that protonation followed by deprotonation gives only **4**. Protonation occurs γ to the nitrile giving both (*E*)- and (*Z*)-propene isomers. Both **1** and **2** produce a 1,2,3-tripyridinium-1-ylindolizine (**6**) on heating. The pK_a's of the conjugate acids of **2** and **4** are 3.2 and −0.8, respectively.

In earlier papers,[1,2] we reported the reaction of pyridines with tetrachlorocyclopropene, TCCP,[3] to form indolizines. This reaction was proposed to involve successive nucleophilic additions of the pyridine to the cyclopropene double bond to form cyclopropyl anions, which could eliminate chloride ion and then be further substituted by additional pyridinium groups. With additional pyridinium substitution, the cyclopropyl anion is increasingly stabilized toward chloride elimination, and competing electrocyclic ring opening can occur to the isomeric substituted allyl anion. A further electrocyclic ring closure involving the allyl anion moiety and a pyridinium substituent can then occur to lead to the indolizine product.[4] Electron-donating substituents on the pyridine were proposed to destabilize the intermediate cyclopropyl anion, resulting in a greater degree of pyridinium-1-yl substitution. With 4-(dimethylamino)pyridine, DMAP, a rather basic pyridine, substitution on TCCP occurs to replace all of the chlorines and results in the formation of the cyclopropene, **1**.[5]

(1) Smith, K. A.; Streitwieser, A., Jr. *J. Org. Chem.* **1983**, *48*, 2629–2630.
(2) Smith, K. A.; Waterman, K. C.; Streitwieser, A., Jr. *J. Org. Chem.* **1985**, *50*, 3360–5.
(3) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2481; *Tetrahedron Lett.* **1963**, 1179–1182.
(4) Sasaki, T.; Kanematsu, K.; Kakehi, A.; Ito, G. *Tetrahedron* **1972**, *28*, 4947–4958.

0022-3263/88/1953-0583$01.50/0