2,5-Cyclohexadien-1-one Photochemistry. Reversible Type B Oxyallyl Zwitterion Formation from Photorearrangements of Bicyclo[3.1.0]hex-3-en-2-ones

Arthur G. Schultz* and John Reilly

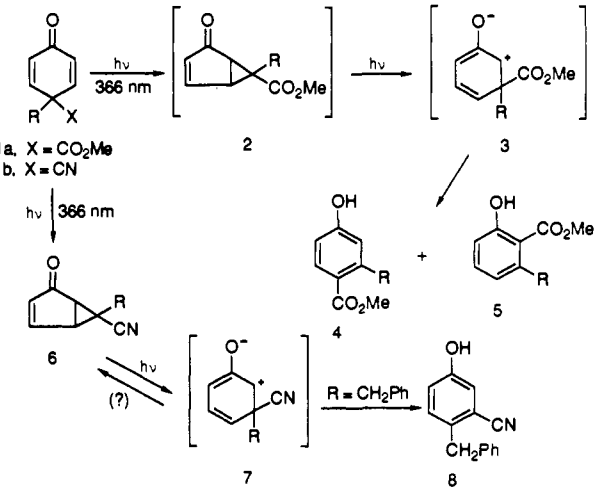
Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590. *Received December 16, 1991*

Abstract: Irradiation of 4-cyano-4-[3′-(2-furyl)propyl]-2,5-cyclohexadien-1-one (**9a**) gave the type B zwitterion–furan cycloadduct **10**. Shorter periods of irradiation of **9a** enabled isolation of an intermediate, 6-cyano-6-[3′-(2-furyl)propyl]bicyclo[3.1.0]-hex-3-en-2-one, which underwent photorearrangement to **10** on further irradiation. Photorearrangement of 2,5-cyclohexadien-1-one **9b** has been shown to give a mixture of diastereomeric bicyclohexenones **11**; irradiation of **9b** or **11** in the presence of furan gave cycloadduct **13**. These observations indicate that the apparent photostability of 6-alkyl-6-cyanobicyclo[3.1.0]hexenones is a result of the absence of efficient pathways for 1,2-rearrangement of the type B zwitterion to phenolic products rather than suppression of zwitterion formation. It is suggested that formation of zwitterion **12** from **11** is reversible. Because the thermal reversion of **12** to **11** is forbidden, this reaction is thought to occur via the excited state of **12**. Novel photorearrangement pathways were discovered for the 4-cyano-3-methoxy-2,5-cyclohexadien-1-ones **14** and **19** which give 2- and 3-methoxy-substituted cycloadducts **17**, **18**, **21**, and **22**. The isolation of **18** and **22** necessitates the formulation of a second type B zwitterion (**27**; Scheme IV) photogenerated from the as yet unobserved 5-methoxybicyclohexenone **25**. In the presence of added furan or a tethered 2-furyl substituent, zwitterion **27** gives cycloadducts; in the absence of a trapping agent, **27** must convert (photochemically) to the observed 4-methoxybicyclohexenones **24**. Analogous behavior has been observed for the 4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-one **28**.

Photorearrangements of 4-alkyl-4-carbomethoxy-2,5-cyclohexadien-1-ones **1a** at 366 nm result in the formation of phenols **4** and **5**.[1] Phenol formation presumably occurs by the well-known type A photorearrangement[2] of **1a** to intermediate bicyclo-[3.1.0]hex-3-en-2-ones **2**, followed by type B photorearrangement[3] of **2** to oxyallyl zwitterions **3** and competing carbomethoxy group rearrangements to C(2) and C(4) of oxyallyl zwitterions **3**.

By contrast, 4-alkyl-4-cyano-2,5-cyclohexadien-1-ones **1b** were found to undergo type A photorearrangement to give isolable bicyclo[3.1.0]hex-3-en-2-ones **6** that do not undergo further photorearrangement to phenols.[1] However, irradiation of the 4-benzyl derivative of **1b** gave **6** (R = CH_2Ph), which photorearranged to 4-benzyl-3-cyanophenol (**8**) on continued irradiation.

These observations suggested that type B zwitterion formation from **1a** and **1b** is reversible and does not lead to phenolic products when groups with poor migratory aptitude are at C(4) of the starting 2,5-cyclohexadien-1-one (e.g., cyano and primary alkyl). Substitution of primary alkyl with the more mobile benzyl group enables zwitterion **7** (R = CH_2Ph) to rearrange to phenol **8**.



Although this explanation is in agreement with experimental observations, it seemed to contradict expectations of reactivity based on theoretical considerations. The type B zwitterion is considered to be a pentadienyl cation, for which the required disrotatory closure to a 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-one is forbidden.[3] However, a four-electron disrotatory cyclization ought to be possible by way of a photochemical pathway.

At the outset of the experiments to be described in this paper, we sought a more definitive test of the reversibility of type B zwitterion formation. It has been demonstrated that 2-furyl substituents tethered at C(4) of the starting 2,5-cyclohexadien-1-one undergo cycloaddition to the type B zwitterion;[4] tethered 3′-azidopropyl and 3′-alkenyl substituents also are effective trapping agents.[4b,5] We expected that cycloaddition studies with a 4-[3′-(2-furyl)propyl] analogue of **1b** would demonstrate that reversible type B zwitterion formation plays a significant role in the photochemistry of bicyclo[3.1.0]hex-3-en-2-ones.

An important discovery concerning the regioselectivity of the type A photorearrangements of 3-methoxy-2,5-cyclohexadien-1-ones was made during the course of this study. For perspective, it is necessary to review type A photorearrangements of 3-methoxy-2,5-cyclohexadien-1-ones.

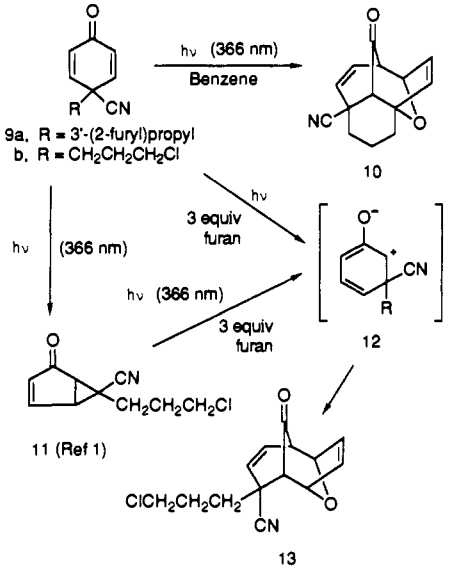
Zimmerman and Pasteris have shown that 3-methoxy-4,4-diphenyl-2,5-cyclohexadien-1-one photorearranges to a 1.4:1 mixture of the 4-methoxy- and the 5-methoxybicyclo[3.1.0]hex-3-en-2-ones.[6] Zimmerman and Pasteris concluded that the 4-methoxybicyclohexenone was derived from the type A zwitterion while the 5-methoxy regioisomer originated directly from the excited-state precursor of the type A zwitterion.

By contrast, 4-carbomethoxy- and 4-cyano-3-methoxy-2,5-cyclohexadien-1-ones undergo photorearrangement at 366 nm to give diastereomeric mixtures of 6-carbomethoxy- and 6-cyano-4-methoxybicyclo[3.1.0]hex-3-en-2-ones; none of the corresponding 5-methoxy regioisomers are detected.[1] Continued irradiation of the bicyclohexenone diastereomers at 366 nm results in photoequilibration to give mainly the 6-*endo*-carbomethoxy- and 6-

(1) Schultz, A. G.; Lavieri, F. P.; Macielag, M.; Plummer, M. *J. Am. Chem. Soc.* **1987**, *109*, 3991.
(2) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527.
(3) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 7806.
(4) (a) Schultz, A. G.; Puig, S.; Wang, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 785. (b) Schultz, A. G.; Macielag, M.; Plummer, M. *J. Org. Chem.* **1988**, *53*, 391.
(5) (a) Schultz, A. G.; Myong, S. O.; Puig, S. *Tetrahedron Lett.* **1984**, *25*, 1011. (b) Schultz, A. G.; Plummer, M. *J. Org. Chem.* **1989**, *54*, 2112.
(6) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4876.

0002-7863/92/1514-5068$03.00/0

Scheme I



endo-cyanobicyclohexenones. Trace amounts of phenolic products slowly begin to accumulate after extended irradiation of the 6-carbomethoxybicyclohexenones at 366 nm, while extended irradiation through Pyrex glassware (≥300 nm) affords phenols as the sole reaction products. In analogy with 6-cyanobicyclohexenone **6** (R = primary alkyl), irradiation of 6-cyano-4-methoxybicyclohexenones does not result in formation of phenols.

It will now be shown from inter- and intramolecular furan–oxyallyl zwitterion cycloaddition studies that 5-methoxybicyclo[3.1.0]hexenones apparently are produced during photolyses of 4-carbomethoxy- and 4-cyano-3-methoxy-2,5-cyclohexadienones, but in the absence of trapping agents, 5-methoxybicyclo[3.1.0]-hexenones photorearrange to the 4-methoxy regioisomers.

Results and Discussion

4-Cyano-Substituted 2,5-Cyclohexadien-1-ones. Cyclohexadienone **9a** was prepared from benzonitrile by procedures already described in detail.[1,4b] Irradiation of **9a** in benzene solution at 366 nm gave 4-cyano-13-oxo-12-oxatetracyclo[6.3.2.1.0]tetradeca-2,9-diene (**10**) along with uncharacterized decomposition products (Scheme I). Flash chromatography of the photoreaction mixture provided the crystalline cycloadduct **10**. The structure of **10** was established by comparisons of spectroscopic data obtained for **10** and an analogue for which an X-ray-determined molecular structure was available.[4a]

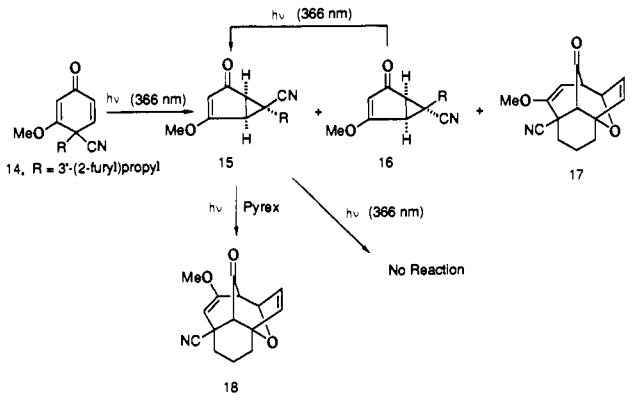
Shorter periods of irradiation of **9a** enabled isolation of a 6-cyano-6-[3'-(2-furyl)propyl]bicyclo[3.1.0]hex-3-en-2-one; this substance underwent photorearrangement to **10** on further irradiation.

It was decided to unequivocally demonstrate that a type B zwitterion (i.e., **12**) is in photochemical equilibrium with 6-alkyl-6-cyanobicyclo[3.1.0]hex-3-en-2-ones. Cyclohexadienone **9b** was selected for study because it had been shown that type A photorearrangement of **9b** at 366 nm gave a mixture of diastereomeric bicyclohexenones **11**.[1] Subsequent irradiation of **11** resulted in a change in the distribution of diastereomers but did not give rise to type B photorearrangement products.

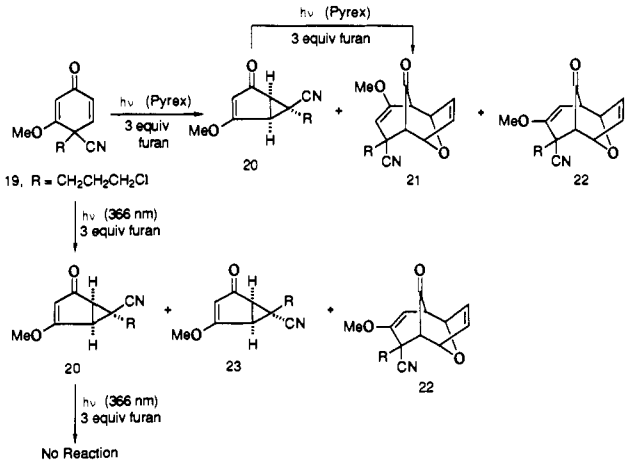
Irradiation of **9b** in the presence of 3 equiv of furan afforded the furan–oxyallyl zwitterion cycloadduct **13**.[6] Furthermore, irradiation of **11** under these same reaction conditions also gave **13**. These observations clearly show that the apparent photostability of 6-alkyl-6-cyanobicyclo[3.1.0]hexenones is a result of the absence of efficient pathways for 1,2-rearrangement of the type B zwitterion to phenolic products rather than suppression of zwitterion formation.

Cyclohexadienone **14** was prepared from 2-methoxybenzonitrile,[1] and irradiation in benzene solution at 366 nm provided bicyclohexenone diastereomers **15** and **16** as well as an intramolecular oxyallyl zwitterion–furan cycloadduct **17** possessing

Scheme II



Scheme III



an unexpected substitution pattern (Scheme II). Separation of the photoproducts proved to be somewhat difficult. Flash chromatography on silica gel afforded recovered cyclohexadienone **14** (11%), the 6-*endo*-cyanobicyclohexenone **15** (18%), and a fraction containing a 1:3 mixture of the 6-*exo*-cyanobicyclohexenone **16** and cycloadduct **17** (40%). Continued irradiation of the mixture of **16** and **17** at 366 nm gave a mixture of isomerized bicyclohexenone **15** and cycloadduct **17**, which now provided pure **17** by flash chromatographic separation.

Bicyclohexenone **15** was found to be stable to irradiation in benzene solution at 366 nm but photorearranged to the intramolecular oxyallyl zwitterion–furan cycloadduct **18** (43%) when irradiated through Pyrex glassware. A control experiment demonstrated that cycloadduct **17** did not photorearrange to **18** (≥300 nm).

The intermolecular oxyallyl zwitterion–furan cycloaddition was examined with 3-methoxy-2,5-cyclohexadien-1-one **19** (Scheme III). Previous studies had shown that **19** photorearranges to bicyclohexenones **20** and **23** on irradiation at 366 nm.[1] Pyrex-filtered irradiation of **19** in benzene solution in the presence of 3 equiv of furan gave 6-*endo*-cyanobicyclohexenone **20** (20%), cycloadduct **21** (21%), and the 3-methoxy-substituted cycloadduct **22** (33%) analogous to the intramolecular cycloadduct **17**. At 366 nm, **19** gave a 3:1:2 mixture of bicyclohexenones **20** and **23** and cycloadduct **22**. The structure of **22** was determined by X-ray crystallographic studies; the molecular structure of **22** is shown in Figure 1.

Control experiments showed that Pyrex-filtered irradiation of bicyclohexenone **20** in the presence of furan gave cycloadduct **21**; none of the 3-methoxy-substituted cycloadduct **22** was detected in the photoreaction mixtures. Furthermore, **20** was recovered unchanged after irradiation at 366 nm in the presence of furan.

It is noteworthy that **22** is formed by intermolecular cycloaddition of furan to the less sterically hindered face of the intermediate type B zwitterion (e.g., **27** in Scheme IV). Presum-

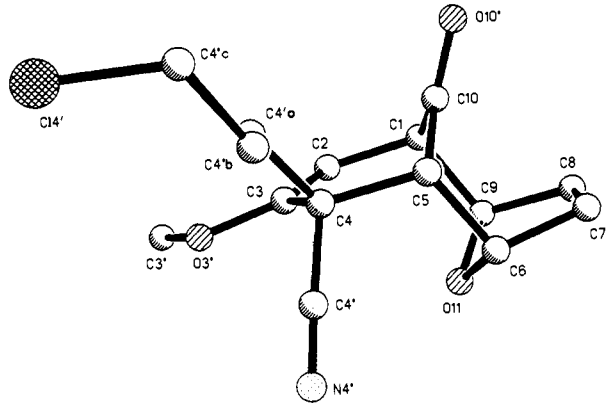
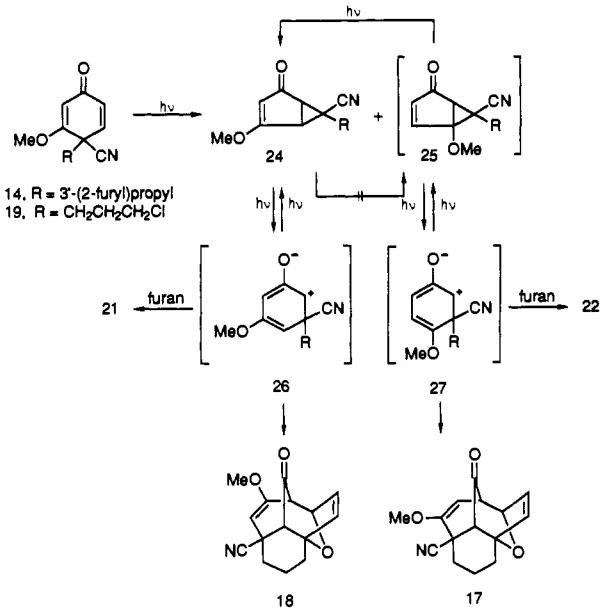


Figure 1. Molecular structure of **22**.

Scheme IV



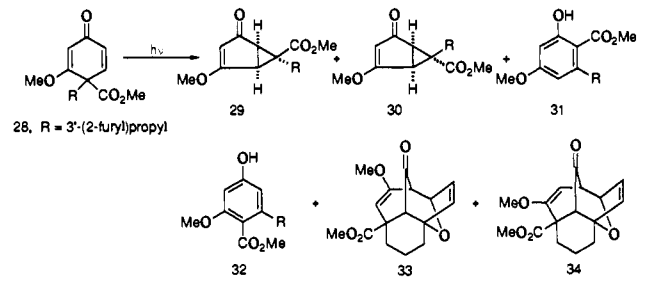
ably, this same configurational relationship is present in **21** and **13**. The complementary stereoselectivities of inter- and intramolecular oxyallyl zwitterion–furan cycloaddition (cf., **10** vs **13**) should be of use in synthetic applications.

Mechanistic Considerations. The isolation of the intramolecular furan–oxyallyl zwitterion cycloadduct **10** from photolysis of **9a** and the intermolecular cycloadduct from **9b** and **11** convincingly demonstrates that type B zwitterion formation can be reversible. On the basis of previously discussed considerations,[3] reversion is thought to occur from an electronically excited state of zwitterion **12**. Although relatively little is known about the absorption characteristics of the type B zwitterion, it has been reported that low-temperature photolyses of lumisantonin derivatives in methyltetrahydrofuran–isopentane glasses generate colored species believed to be the reaction intermediates for photoproduct formation.[7] If the lumisantonin transients are characteristic of type B intermediates, then it is clear that zwitterions such as **12**, which are not prone to undergo rearrangement to phenols, will compete with **11** for light absorption. Alternatively, **12** might revert to **11** via a pathway involving intermolecular energy transfer.

The isolation of oxyallyl zwitterion–furan cycloadducts **17** and **22** necessitates the formulation of a second type B zwitterion, namely, **27** (Scheme IV). Type A photorearrangement of **14** and **19** apparently gives not only the isolable 4-methoxybicyclo[3.1.0]hexenone **24** but also the 5-methoxy regioisomer **25**. Bicyclohexenone **25** has not been detected from irradiations of **19** in the absence of furan, which implies that **25** must undergo

(7) (a) Fisch, M. H.; Richards, J. H. *J. Am. Chem. Soc.* **1968**, *90*, 1547. (b) Fisch, M. H. *J. Chem. Soc., Chem. Commun.* **1969**, 1472.

Scheme V



photorearrangement to the 4-methoxybicyclohexenone **24**.

To account for the formation of cycloadducts **17** and **22**, it is proposed that bicyclohexenone **25** also photorearranges to the type B zwitterion **27**. If the substituent R in **27** is the 3'-(2-furyl)propyl group, then intramolecular oxyallyl zwitterion–furan cycloaddition generates **17**. In the absence of an intramolecular trapping agent, **27** reverts to **25**, presumably by way of a photochemical pathway (cf., **12** → **11**). In the presence of furan, **27** (R = $CH_2CH_2CH_2Cl$) is converted to cycloadduct **22**.

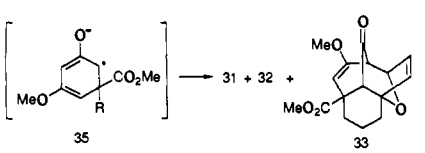
Although it appears clear that bicyclohexenone **25** photoconverts to bicyclohexenone **24**, the complementary photorearrangement of **24** to **25** most certainly does not occur. This was demonstrated in two ways: (1) bicyclohexenone **15** was found to be photostable at 366 nm and photoreactive at ≥300 nm to give only cycloadduct **18**, and (2) Pyrex-filtered irradiation of **20** in the presence of furan gave **21**, but not the rearranged cycloadduct **22**.

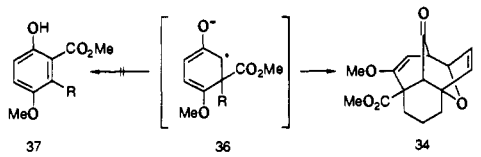
Formation of oxyallyl zwitterion **26** also is reversible. Thus, although bicyclohexenone **20** appears to be photostable at 366 nm and ≥300 nm in the absence of furan, **20** does provide cycloadduct **21** on irradiation at ≥300 nm in the presence of furan.

4-Carbomethoxy-Substituted 2,5-Cyclohexadien-1-ones. We have reported that 4-[3'-(2-furyl)propyl]-3-methoxy-4-(methoxycarbonyl)cyclohexa-2,5-dien-1-one (**28**) photorearranges to bicyclohexenone **29** and phenol **31**.[4b] However, the yields for isolation of **29** and **31** were low, and an examination of ^1H NMR spectra of photoreaction mixtures indicated that several other components were present. Since it was important to determine the role of 5-methoxybicyclohexenones in the photochemistry of 4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-ones, photorearrangements of **28** were carefully reexamined (Scheme V).

Irradiation of cyclohexadienone **28** in benzene solution (Pyrex) and chromatography of the reaction mixture on silica gel gave bicyclohexenones **29** (30%) and **30** (2%), phenols **31** (19%) and **32** (2%), and cycloadducts **33** (<5%) and **34** (14%). A similar distribution of photoproducts was obtained from extended irradiation of **28** at 366 nm. Pyrex-filtered irradiation of **28** taken to complete consumption of intermediate bicyclohexenones **29** and **30** provided phenols **31** (34%) and **32** (5%) and cycloadducts **33** (10%) and **34** (23%). No direct evidence for the presence of a 5-methoxybicyclo[3.1.0]hex-3-en-2-one could be obtained from this or other photoreactions of **28**. Finally, irradiation of bicyclohexenone **29** through Pyrex glassware gave phenols **31** and **32** and cycloadduct **33**, but not cycloadduct **34**.

These data demonstrate that intramolecular furan cycloadducts are obtained from tandem photorearrangements of 4-carbomethoxy-2,5-cyclohexadien-1-one **28**, albeit in poor yield. It is proposed that intermediate bicyclohexenones **29** and **30** photorearrange to zwitterion **35**, the precursor of phenols **31** and **32** and cycloadduct **33**. In analogy with the mechanism advanced in Scheme IV, it appears that a 5-methoxybicyclohexenone also is photogenerated from cyclohexadienone **28**. Subsequent photoisomerization of the 5-methoxybicyclohexenone to zwitterion **36** and intramolecular cycloaddition of the zwitterion to the tethered furan would give the rearranged cycloadduct **34**. It is





37 36 34

noteworthy that rearrangement of **36** to phenol **37** was not detected.

Conclusion

Cycloaddition studies have shown that photorearrangements of 6-alkyl-6-cyanobicyclo[3.1.0]hex-3-en-2-ones to the type B zwitterion (e.g., **11** → **12**) are reversible. Bicyclohexenone **11** was ideally substituted for this study because primary alkyl and cyano substitution in zwitterion **12** does not enable 1,2-rearrangement to phenolic products. Reversibility of type B zwitterion formation from 6-alkyl-6-cyano- and 6-alkyl-6-carbomethoxy-4-methoxybicyclo[3.1.0]hex-3-en-2-ones also has been demonstrated (Schemes IV and V).

A quite remarkable additional discovery is the photorearrangement of the putative 5-methoxybicyclo[3.1.0]hex-3-en-2-ones **25** to the 4-methoxy regioisomers **24**. How do these fascinating photorearrangements occur?

Photorearrangement of **25** to **24** might occur by a photoreversion to the type A zwitterion **38** or a related species via cleavage of cyclopropane bond a in **25** (Scheme VI). Alternatively, **25** might be converted to an intermediate 2-methoxybicyclo[2.1.1]hex-2-en-5-one **39**[8] by a photochemical vinyl cyclopropane rearrangement involving cleavage of cyclopropane bond b.[9] We have already shown that bond a and/or b cleavages are responsible for interconversions of diastereomeric 4-methoxybicyclo[3.1.0]-hex-3-en-2-ones.[1] It is presumed that **39** would convert to **24** by a photochemical pathway involving cleavage of bond a.

Although the formation of mixtures of regioisomeric oxyallyl zwitterion–furan cycloadducts from 3-methoxy-2,5-cyclohexadien-1-ones limits synthetic utility, it should be noted that 2,5-cyclohexadien-1-ones with other substitution patterns do provide cycloadducts in excellent yield.[4,5]

Experimental Section

6-Cyano-6-[3′-(2-furyl)propyl]-1-methoxy-1,4-cyclohexadiene. A solution of 2-methoxybenzonitrile (593 mg, 4.45 mmol) in dry THF (10 mL) and *tert*-butyl alcohol (330 mg, 4.45 mmol) was cooled to −78 °C. Liquid anhydrous ammonia (60 mL) was added to the reaction mixture. Lithium (68 mg, 9.8 mmol, 2.2 equiv) was added to the stirred solution in small pieces. The solution turned blue. The mixture was stirred for 10 min at −78 °C, and piperylene was added until the blue coloration disappeared. To the ammonia solution at −78 °C was added 2-(3-iodopropyl)furan (1.05 g, 4.45 mmol). After the solution was stirred at −78 °C for 1.5 h, solid ammonium chloride was added, and the reaction mixture was allowed to warm to room temperature. Water and ether were added, and the organic layer was washed (2× each) with a solution of sodium thiosulfate (~10%), water, and brine and dried over anhydrous magnesium sulfate. Removal of solvent in vacuo afforded a yellow oil (1.06 g). Flash chromatography (silica gel, hexane–ethyl acetate, 7:1) gave the cyclohexadiene (822 mg, 76%) as an oil: ^{1}H NMR ($CDCl_3$) δ 1.45–1.90 (m, 3 H), 2.12 (m, 1 H), 2.63 (t, 2 H, J = 7 Hz), 2.65–2.98 (m, 2 H), 3.62 (s, 3 H), 4.88 (t, 1 H, J = 3 Hz), 5.56 (dt, 1 H, J = 10 Hz, J = 2 Hz), 5.93–6.07 (m, 2 H), 6.28 (t, 1 H, J = 2 Hz), 7.30 (d, 1 H, J = 1 Hz); IR (film) 2950, 2240, 1783, 1704, 1600 cm^{-1}; CIMS, m/z (relative intensity) 244 (M^+ + 1, 53), 217 (100).

4-Cyano-4-[3′-(2-furyl)propyl]-3-methoxy-2,5-cyclohexadien-1-one (14). To a stirred solution of 6-cyano-6-[3′-(2-furyl)propyl]-1-methoxy-1,4-cyclohexadiene (172 mg, 0.707 mmol) in benzene (20 mL) at 0 °C was added Celite (600 mg) and pyridinium dichromate (666 mg, 1.77 mmol). To this slurry was added 90% *tert*-butyl hydroperoxide (160 mg, 1.77 mmol), and the resulting mixture was stirred at 0 °C for 1.5 h and warmed to room temperature and stirred for 1.5 h. The reaction mixture was filtered through a pad of Celite, the solids were washed thoroughly with ethyl acetate, and the filtrate was concentrated in vacuo to give a brown oil. Flash chromatography (silica gel, hexane–ethyl acetate, 4:1) gave the cyclohexadienone (92 mg, 50%) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.45–1.75 (m, 2 H), 2.05–2.35 (m, 2 H), 2.67 (t, 2 H, J = 7 Hz), 3.86 (s, 3 H), 5.73 (s, 1 H), 6.01 (d, 1 H, J = 3 Hz), 6.30 (t, 1 H, J = 2 Hz), 6.39 (d, 1 H, J = 10 Hz), 6.60 (d, 1 H, J = 10 Hz), 7.32 (d, 1 H, J = 1 Hz); IR (film) 2955, 2245, 1715, 1660, 1605 cm^{-1}; CIMS, m/z (relative intensity) 258 (M^+ + 1, 57), 109 (83), 81 (100). UV (MeOH): 366 nm (ϵ = 9), 300 (813); λ_{max} 272 (4069), 220 (12313).

Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.03; H, 5.88. Found: C, 69.98; H, 5.92.

6-Cyano-6-[3′-(2-furyl)propyl]-1,4-cyclohexadiene: prepared from benzonitrile (2.23 g, 21.7 mmol) as described for 6-cyano-6-[3′-(2-furyl)propyl]-1-methoxy-1,4-cyclohexadiene. Flash chromatography (silica gel, hexane–ethyl acetate, 10:1) gave the cyclohexadiene (3.13 g, 68%) as an oil: ^{1}H NMR ($CDCl_3$) δ 1.65–1.87 (m, 4 H), 2.55–2.88 (m, 4 H), 5.66 (dt, 2 H, J = 10 Hz, J = 2 Hz), 5.93–6.05 (m, 3 H), 6.30 (m, 1 H), 7.33 (s, 1 H); IR (film) 3040, 2958, 2218, 1597, 1509 cm^{-1}; CIMS, m/z (relative intensity) 214 (M^+ + 1, 100), 187 (99).

4-Cyano-4-[3′-(2-furyl)propyl]-2,5-cyclohexadien-1-one (9a): prepared from 6-cyano-6-[3′-(2-furyl)propyl]-1,4-cyclohexadiene (3.2 g, 15 mmol) as described for 4-cyano-4-[3′-(2-furyl)propyl]-3-methoxy-2,5-cyclohexadien-1-one. Flash chromatography (silica gel, hexane–ethyl acetate, 7:3) gave the cyclohexadienone (910 mg, 27%) as an oil: ^{1}H NMR ($CDCl_3$) δ 1.72–1.93 (m, 2 H), 1.97–2.11 (m, 2 H), 2.72 (t, 2 H, J = 7 Hz), 6.04 (d, 1 H, J = 3 Hz), 6.32 (t, 1 H, J = 2 Hz), 6.49 (d, 2 H, J = 10 Hz), 6.86 (d, 2 H, J = 10 Hz), 7.34 (d, 1 H, J = 2 Hz); IR (film) 2945, 2219, 1728, 1668, 1633, 1506 cm^{-1}; CIMS, m/z (relative intensity) 228 (M^+ + 1, 100), 109 (31). UV (MeOH): 366 nm (ϵ = 11), 300 (188); λ_{max} 228 (11458).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 74.00; H, 5.77. Found: C, 73.72; H, 5.61.

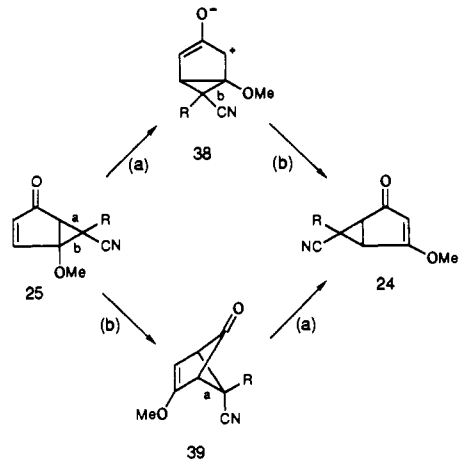
6-Cyano-6-[3′-(2-furyl)propyl]-4-methoxybicyclo[3.1.0]hex-3-en-2-ones (15 and 16) and 4-Cyano-3-methoxy-13-oxo-12-oxatetracyclo-[6.3.2.1.0]tetradeca-2,9-diene (17). **14** (180 mg, 0.700 mmol) in benzene (25 mL) was irradiated through uranyl glass (366 nm) for 7 h. Concentration of the reaction mixture gave a yellow foam (178 mg). Flash chromatography (silica gel, hexane–ethyl acetate, 4:1) provided **14** (20 mg, 11%).

15 was obtained as an oil (33 mg, 18%): ^{1}H NMR ($CDCl_3$) δ 1.55–1.68 (m, 2 H), 1.92–2.08 (m, 2 H), 2.32 (dd, 1 H, J = 5 Hz, J = 1 Hz), 2.55 (dd, 1 H, J = 5 Hz, J = 1 Hz), 2.74 (t, 2 H, J = 7 Hz), 3.91 (s, 3 H), 5.06 (t, 1 H, J = 1 Hz), 6.05 (dd, 1 H, J = 3 Hz, J = 1 Hz), 6.31 (t, 1 H, J = 2 Hz), 7.33 (d, 1 H, J = 1 Hz); IR (film) 3060, 2940, 2240, 1680, 1575 cm^{-1}; CIMS, m/z (relative intensity) 258 (M^+ + 1, 100). UV (MeOH): 366 nm (ϵ = 11), 300 (934); λ_{max} 266 (7876), 218 (9655).

An acceptable elemental analysis could not be obtained.

16 and **17** were obtained as an inseparable 1:3 mixture; ^{1}H NMR analysis (72 mg, 40%). **16**: ^{1}H NMR ($CDCl_3$) δ 1.55–2.05 (m, 4 H), 2.60–2.87 (m, 3 H), 2.94 (d, 1 H, J = 5 Hz), 3.83 (s, 3 H), 4.97 (s, 1 H), 6.05 (d, 1 H, J = 3 Hz), 6.31 (m, 1 H), 7.33 (s, 1 H). Continued irradiation of the mixture of **16** and **17** in deaerated benzene (5 mL) through uranyl glass (366 nm) for 3 h, followed by concentration of the reaction mixture, provided a mixture of **15** and **17**. Following flash chromatography (silica gel, hexane–ethyl acetate, 4:1) an analytical sample of **17** was prepared by recrystallization from hexane–ethyl acetate to give a white solid (mp 160–161 °C): ^{1}H NMR ($CDCl_3$) δ 1.62–2.07 (m, 5 H), 2.51 (d, 1 H, J = 2 Hz), 2.69 (m, 1 H), 3.02 (dt, 1 H, J =

Scheme VI



38 25 24 39

(8) For rearrangements of bicyclo[2.1.1]hex-2-enes, see: (a) Masamune, S.; Takada, S.; Nakatsuka, N.; Vukov, R.; Cain, E. N. *J. Am. Chem. Soc.* **1969**, *91*, 4322. (b) Roth, W. R.; Friedrich, A. *Tetrahedron Lett.* **1969**, 2607. (c) Roth, R. J.; Katz, T. J. *J. Org. Chem.* **1980**, *45*, 961.

(9) Schultz, A. G.; Green, N. J. *J. Am. Chem. Soc.* **1992**, *114*, 1824.

6 Hz, J = 2 Hz), 3.69 (s, 3 H), 4.59 (t, 1 H, J = 1 Hz), 4.92 (d, 1 H, J = 6 Hz), 6.13 (d, 1 H, J = 6 Hz), 6.34 (dd, 1 H, J = 6 Hz, J = 2 Hz); IR (CCl_4) 2965, 2240, 1732, 1632 cm^{-1}; CIMS, m/z (relative intensity) 258 (M^+ + 1, 100), 231 (3).

Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.03; H, 5.88. Found: C, 70.01; H, 5.76.

Irradiation of Bicyclohexenone 15 at 366 nm. 15 (14 mg, 0.05 mmol) in benzene (5 mL) was irradiated through uranyl glass for 15 h. Concentration of the reaction mixture gave **15** as determined by ^1H NMR analysis of the crude product.

4-Cyano-2-methoxy-13-oxo-12-oxatetracyclo[6.3.2.1.0]tetradeca-2,9-diene (18). 15 (30 mg, 0.12 mmol) in benzene (20 mL) was irradiated through Pyrex glass (>300 nm) for 7.5 h. Concentration of the reaction mixture gave a yellow oil (30 mg). Flash chromatography (silica gel, hexane–ethyl acetate, 4:1) gave **18** (13 mg, 43%). An analytical sample was prepared by recrystallization from hexane–ethyl acetate to give a white solid (mp 170–171 °C): ^1H NMR ($CDCl_3$) δ 1.58–1.80 (m, 3 H), 1.95–2.10 (m, 2 H), 2.23 (m, 1 H), 2.55 (s, 1 H), 3.07 (m, 1 H), 3.66 (s, 3 H), 4.73 (s, 1 H), 4.83 (m, 1 H), 6.21 (d, 1 H, J = 6 Hz), 6.35 (dd, 1 H, J = 6 Hz, J = 2 Hz); IR (CCl_4) 2938, 2862, 2235, 1725, 1638 cm^{-1}; CIMS, m/z (relative intensity) 258 (M^+ + 1, 23), 231 (100).

Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.03; H, 5.88. Found: C, 70.05; H, 5.74.

Irradiation of Cycloadduct 17 at >300 nm. 17 (14 mg, 0.05 mmol) in benzene (5 mL) was irradiated through Pyrex glass for 20 h. Concentration of the reaction mixture gave **17** as determined by ^1H NMR analysis of the crude product.

6-(3′-Chloropropyl)-6-cyano-4-methoxybicyclo[3.1.0]hex-3-en-2-one (20), 4-(3′-Chloropropyl)-4-cyano-3-methoxy-11-oxo-10-oxatricyclo-[3.3.2.1]undeca-2,7-diene (22), and 4-(3′-Chloropropyl)-4-cyano-2-methoxy-11-oxo-10-oxatricyclo[3.3.2.1]undeca-2,7-diene (21). 19 (328 mg, 1.45 mmol) in benzene (25 mL) and furan (0.33 mL, 4.4 mmol) was irradiated through Pyrex glass for 16 h. Concentration of the reaction mixture gave a yellow oil (449 mg). Flash chromatography (silica gel, hexane–ethyl acetate, 7:3) provided **20** (66 mg, 20%); the ^1H NMR spectrum was identical to that previously described for **20**.[1]

21 was obtained as an oil (89 mg, 21%). An analytical sample of **21** was prepared by crystallization from hexane–ethyl acetate to give a white solid (mp 127–128 °C): ^1H NMR ($CDCl_3$) δ 1.85–2.10 (m, 4 H), 2.60 (s, 1 H), 2.98 (t, 1 H, J = 2 Hz), 3.59 (t, 2 H, J = 6 Hz), 3.66 (s, 3 H), 4.84 (s, 1 H), 4.96 (t, 1 H, J = 2 Hz), 5.31 (t, 1 H, J = 2 Hz), 6.36 (dd, 1 H, J = 6 Hz, J = 2 Hz), 6.45 (dd, 1 H, J = 6 Hz, J = 2 Hz); IR (film) 2975, 2235, 1735, 1655 cm^{-1}; CIMS, m/z (relative intensity) 294 (M^+ + 1, 33), 267 (100).

Anal. Calcd for $C_{15}H_{16}ClNO_3$: C, 61.33; H, 5.49. Found: C, 61.23; H, 5.35.

22 was obtained as an oil (136 mg, 32%). An analytical sample was prepared by crystallization from hexane–ethyl acetate to give a white solid (mp 155–156 °C): ^1H NMR ($CDCl_3$) δ 1.80–2.30 (m, 4 H), 2.62 (t, 1 H, J = 2 Hz), 2.95 (dt, 1 H, J = 7 Hz, J = 2 Hz), 3.57 (t, 2 H, J = 6 Hz), 3.71 (s, 3 H), 4.73 (t, 1 H, J = 2 Hz), 4.95 (d, 1 H, J = 7 Hz), 5.28 (t, 1 H, J = 2 Hz), 6.28 (dd, 1 H, J = 6 Hz, J = 2 Hz), 6.45 (dd, 1 H, J = 6 Hz, J = 2 Hz); IR (film) 2975, 2240, 1730, 1645 cm^{-1}; CIMS, m/z (relative intensity) 294 (M^+ + 1, 44), 267 (7), 226 (100).

Anal. Calcd for $C_{15}H_{16}ClNO_3$: C, 61.33; H, 5.49. Found: C, 61.26; H, 5.56.

Irradiation of Bicyclohexenone 20 at 366 nm. 20 (83 mg, 0.37 mmol) in benzene (15 mL) and furan (75 mg, 1.1 mmol) was irradiated through uranyl glass for 4.75 h. Concentration of the reaction mixture gave **20** as an oil (81 mg) as determined by ^1H NMR analysis.

Irradiation of Bicyclohexenone 20 at >300 nm. 20 (83 mg, 0.37 mmol) in benzene (15 mL) and furan (75 mg, 1.1 mmol) was irradiated through Pyrex glass for 4.75 h. Concentration of the reaction mixture gave a mixture of **20** and **21** (3:1) as an oil (75 mg) as determined by ^1H NMR analysis. Minor amounts (<10%) of uncharacterized products are visible in the NMR spectrum.

Irradiation of Cyclohexadienone 19 at 366 nm. 19 (290 mg, 1.29 mmol) in benzene (25 mL) and furan (263 mg, 3.87 mmol) was irradiated through uranyl glass for 4.5 h. Concentration of the reaction mixture gave a mixture of **20**, **23**, and **22** (3:1:2) as an oil (333 mg) as determined by ^1H NMR analysis. The ^1H NMR spectrum of **23** was identical to that previously reported.[1]

Irradiation of Cyclohexadienone 9a at 366 nm. 9a (105 mg) in benzene (25 mL) was irradiated through uranyl glass for 3 h. Concentration of the reaction mixture followed by flash chromatography (silica gel, hexane–ethyl acetate, 3:1) gave **10** (27 mg, 26%). An analytical sample was prepared by recrystallization from hexane–ethyl acetate to give a white solid (mp 149–150 °C): ^1H NMR ($CDCl_3$) δ 1.65–2.15 (m, 5 H), 2.27 (m, 1 H), 2.57 (s, 1 H), 3.06 (m, 1 H), 4.69 (t, 1 H, J = 2 Hz), 5.87 (dd, 1 H, J = 9 Hz, J = 1 Hz), 6.06 (dd, 1 H, J = 9 Hz, J = 6 Hz), 6.19 (d, 1 H, J = 6 Hz), 6.34 (dd, 1 H, J = 6 Hz, J = 2 Hz); IR ($CHCl_3$) 3031, 2960, 2241, 1733 cm^{-1}; CIMS, m/z (relative intensity) 228 (M^+ + 1, 100).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77. Found: C, 74.07; H, 5.68.

6-*endo*-Cyano-6-[3′-(2-furyl)propyl]bicyclo[3.1.0]hex-3-en-2-one (8 mg, 8%) also was isolated (oil): ^1H NMR ($CDCl_3$) δ 1.52–1.74 (m, 2 H), 1.90–2.08 (m, 2 H), 2.29 (d, 1 H, J = 5 Hz), 2.67–2.77 (m, 3 H), 6.02–6.10 (m, 2 H), 6.29 (t, 1 H, J = 2 Hz), 7.31 (s, 1 H), 7.59 (m, 1 H); IR (film) 2928, 2238, 1703, 1571 cm^{-1}; EIMS, m/z (relative intensity) 227 (M^+, 1), 147 (67), 81 (100).

Irradiation of 6-*endo*-Cyano-6-[3′-(2-furyl)propyl]bicyclo[3.1.0]hex-3-en-2-one at >300 nm. The bicyclohexenone (10.5 mg) in benzene (15 mL) was irradiated through Pyrex glass for 5 h. Concentration of the reaction mixture gave **10** as determined by ^1H NMR analysis.

Irradiation of 6-*endo*-Cyano-6-[3′-(2-furyl)propyl]bicyclo[3.1.0]hex-3-en-2-one at 366 nm. The bicyclohexenone (8 mg) in chloroform-*d* (1.5 mL) was irradiated through uranyl glass for 3.25 h. ^1H NMR analysis of the reaction mixture showed that **10** was the major photoproduct.

Irradiation of Cyclohexadienone 28 at >300 nm. 28 (595 mg) in benzene (80 mL) was irradiated through Pyrex glass for 9 h. Removal of solvent in vacuo gave 567 mg of an oil. Flash chromatography (silica gel, hexane–ethyl acetate, 4:1) gave phenol **31** (111 mg, 19%) as an oil: ^1H NMR ($CDCl_3$) δ 1.88 (qn, 2 H, J = 8 Hz), 2.67 (t, 2 H, J = 7 Hz), 2.90 (t, 2 H, J = 8 Hz), 3.80 (s, 3 H), 3.86 (s, 3 H), 6.00 (d, 1 H, J = 3 Hz), 6.27–6.31 (m, 2 H), 6.34 (d, 1 H, J = 3 Hz), 7.31 (d, 1 H, J = 2 Hz), 11.74 (s, 1 H, D_2O exchangeable); IR (film) 3350–2820, 1722 (weak) 1645, 1612, 1564 cm^{-1}; CIMS, m/z (relative intensity) 291 (M^+ + 1, 100).

Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.14; H, 6.17.

Phenol **32** (13 mg, 2%) also was obtained as an oil: ^1H NMR ($CDCl_3$) δ 1.90 (qn, 2 H, J = 8 Hz), 2.56 (t, 2 H, J = 8 Hz), 2.64 (t, 2 H, J = 7 Hz), 3.77 (s, 3 H), 3.84 (s, 3 H), 5.17 (br s, 1 H, D_2O exchangeable), 5.98 (d, 1 H, J = 3 Hz), 6.24–6.31 (m, 3 H), 7.30 (m, 1 H); IR (film) 3560–3100, 2952, 1698, 1600 cm^{-1}; CIMS, m/z (relative intensity) 291 (M^+ + 1, 100).

Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.03; H, 6.09.

Cycloadduct **34** (84 mg, 14%) was obtained as a solid (mp 126–128 °C); ^1H NMR ($CDCl_3$) δ 1.60–2.14 (m, 5 H), 2.28 (m, 1 H), 2.35 (d, 1 H, J = 2 Hz), 2.94 (m, 1 H), 3.60 (s, 3 H), 3.65 (s, 3 H), 4.60 (dd, 1 H, J = 3 Hz, J = 2 Hz), 4.86 (d, 1 H, J = 7 Hz), 6.06 (d, 1 H, J = 6 Hz), 6.30 (dd, 1 H, J = 6 Hz, J = 2 Hz); IR (film) 2950, 1720, 1635 cm^{-1}; CIMS, m/z (relative intensity) 291 (M^+ + 1, 100), 259 (23).

Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.20; H, 6.25. Found: C, 66.26; H, 6.12.

Cycloadduct **33** (<5%) was obtained as a solid (mp 117–119 °C): ^1H NMR ($CDCl_3$) δ 1.48–2.09 (m, 6 H), 2.76 (s, 1 H), 2.90 (d, 1 H, J = 2 Hz), 3.60 (s, 3 H), 3.64 (s, 3 H), 4.75–4.80 (m, 2 H), 6.15 (d, 1 H, J = 6 Hz), 6.27 (d, 1 H, J = 6 Hz); IR (film) 2950, 2928, 1730, 1635 cm^{-1}; CIMS, m/z (relative intensity) 291 (M^+ + 1, 100).

Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.20; H, 6.25. Found: C, 66.24; H, 6.15.

Bicyclohexenone **29** (178 mg, 30%) was obtained as an oil with spectral data consistent with those previously reported.[4b]

Bicyclohexenone **30** (11 mg, 2%) was obtained as an oil: ^1H NMR ($CDCl_3$) δ 1.55–2.03 (m, 4 H), 1.54–1.68 (m, 3 H), 2.86 (dd, 1 H, J = 6 Hz, J = 1 Hz), 3.70 (s, 3 H), 3.77 (s, 3 H), 4.91 (t, 1 H, J = 1 Hz), 5.97 (d, 1 H, J = 3 Hz), 6.26 (dd, 1 H, J = 3 Hz, J = 2 Hz), 7.28 (d, 1 H, J = 2 Hz); IR (film) 2950, 1725, 1690, 1588, 1440 cm^{-1}; CIMS, m/z (relative intensity) 291 (M^+ + 1, 100).

Irradiation of Cyclohexadienone 28 at 366 nm. 28 (556 mg) in benzene (80 mL) was irradiated through uranyl glass for 18 h. Removal of solvent in vacuo gave 528 mg of an oil. Flash chromatography (silica gel, hexane–ethyl acetate, 4:1) gave **31** (38 mg, 6%), **34** (106 mg, 19%), **33** (15 mg, 3%), **29** (246 mg, 44%), and **30** (25 mg, 4%).

Irradiation of Bicyclohexenone 29 at 366 nm. 29 (25 mg) in benzene (5 mL) was irradiated through uranyl glass for 8 h. Removal of solvent in vacuo gave 32 mg of an oil. No cycloaddition was visible from analysis of the crude ^1H NMR spectrum. Preparative TLC (silica gel, hexane–ethyl acetate, 1:2) gave **29** (15 mg, 62%).

Irradiation of Bicyclohexenone 29 at >300 nm. 29 (246 mg) in benzene (80 mL) was irradiated through Pyrex glass for 22 h. Removal of solvent in vacuo gave 239 mg of an oil. Flash chromatography (silica gel, hexane–ethyl acetate, 4:1) gave **31** (119 mg, 48%), **32** (26 mg, 11%), **33** (34 mg, 14%), and **29** (45 mg, 18%).

Extended Irradiation of Dienone 28 at >300 nm. 28 (543 mg) in benzene (80 mL) was irradiated through Pyrex glass for 56 h. Removal of solvent in vacuo gave 558 mg of an oil. Flash chromatography (silica

gel, hexane–ethyl acetate, 4:1) gave **31** (186 mg, 34%), **32** (26 mg, 5%), **34** (124 mg, 23%), and **33** (57 mg, 10%).

4-(3'-Chloropropyl)-4-cyano-11-oxo-10-oxatricyclo[3.3.2.1]undeca-2,7-diene (13). **9b** (244 mg, 1.25 mmol) in benzene (80 mL) and furan (255 mg, 3.75 mmol) was irradiated through uranyl glass for 18 h. Removal of solvent in vacuo gave 286 mg of an oil. Flash chromatography (silica gel, hexane–ethyl acetate, 5:1) followed by preparative TLC (silica gel, hexane–ethyl acetate, 1:1) gave **13** (70 mg, >85% pure, <20% yield) and an unidentified byproduct. An analytical sample of **13** was prepared by crystallization from pentane–ethyl acetate to give a white solid (mp 108–109 °C): ^{1}H NMR ($CDCl_3$) δ 1.81–2.04 (m, 4 H), 2.61 (s, 1 H), 2.96 (m, 1 H), 3.56 (t, 2 H, J = 6 Hz), 4.80 (s, 1 H), 5.30 (s, 1 H), 5.90–6.08 (m, 2 H), 6.31 (dd, 1 H, J = 6 Hz, J = 1 Hz), 6.42 (dd, 1 H, J = 6 Hz, J = 1 Hz); IR (film) 2968, 2239, 1719 cm^{-1}; CIMS, m/z (relative intensity) 264 (M^+ + 1, 100), 237 (39), 196 (27).

Anal. Calcd for $C_{14}H_{14}ClNO_2$: C, 63.76; H, 5.35. Found: C, 63.87; H, 5.27.

Irradiation of Bicyclohexenone 11 at 366 nm. **11** (43 mg, 0.22 mmol) in benzene (7 mL) and furan (45 mg, 0.66 mmol) was irradiated through uranyl glass for 3.5 h. Removal of solvent in vacuo gave 61 mg of an oil. Flash chromatography (silica gel, hexane–ethyl acetate, 2:1) followed by preparative TLC (silica gel, hexane–ethyl acetate, 1:1) gave **13** (13 mg, 22%).

Irradiation of Bicyclohexenone 11 at >300 nm. **11** (34 mg, 0.17 mmol) in benzene (7 mL) and furan (35 mg, 0.52 mmol) was irradiated through Pyrex glass for 1.5 h. Removal of solvent in vacuo gave 38 mg of an oil. Flash chromatography (silica gel, hexane–ethyl acetate, 2:1) followed by preparative TLC (silica gel, hexane–ethyl acetate, 1:1) gave **13** (7 mg, 16%).

Acknowledgment. This work was supported by the National Institute of General Medical Science (Grant GM 26568). We thank Dr. F. S. Tham for the X-ray crystallographic structure determination.

Supplementary Material Available: Tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic parameters, and hydrogen atom coordinates for **22** (8 pages). Ordering information is given on any current masthead page.

Stereochemical Analysis of Sulfoxides Obtained by Diverted Desaturation

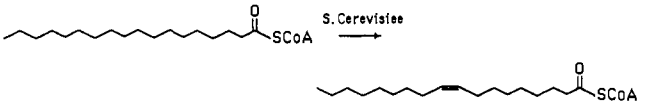
Peter H. Buist* and Dale M. Marecak

Contribution from the Department of Chemistry, Carleton University, Ottawa, Ontario, Canada K1S 5B6. *Received December 2, 1991*

Abstract: We have shown that the Δ^9-desaturase of *Saccharomyces cerevisiae* can behave as a regio- and enantioselective oxygenating agent. The stereochemistry of oxygenation matches that of hydrogen removal in the desaturation process. Thus methyl 9-thiastearate *S*-oxide (>96% ee), obtained via incubation of the corresponding sulfide with *S. cerevisiae* ATCC 12341, was shown to possess the *R* configuration. (*R*)-Methyl 10-thiastearate *S*-oxide (91% ee) was produced from the corresponding sulfide via the same catalytic system although less efficiently. (*S*)-(+)-α-Methoxyphenylacetic acid was used as a chiral NMR shift reagent to determine the optical purity and absolute configuration of these quasisymmetrical dialkyl sulfoxides. (*S*)-*S*-Benzyl-8-mercaptooctanoic acid methyl ester *S*-oxide was obtained by Δ^9-desaturase-mediated sulfoxidation in 40–50% isolated yield and with high enantioselectivity (>98% ee). The absolute configuration was established by synthesizing both optical antipodes of benzyl decyl sulfoxide from the corresponding diastereomeric menthyl phenylmethanesulfinates. The correlation was then established by polarimetry, circular dichroism, and chiral shift reagent ^{1}H NMR. *S*-Benzyl-9-mercaptononanoic acid methyl ester *S*-oxide (88% ee) was produced far less efficiently and was also shown to have the *S* configuration. In both the dialkyl and benzyl series, sulfoxidation at the 9-position is consistently more efficient than at the 10-position, which seems to indicate that dehydrogenation of stearoyl CoA is initiated at C-9.

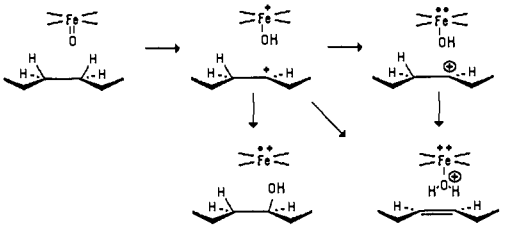
Introduction

As part of a research program directed at understanding unusual enzymatic processes, we have been interested in a "superfamily" of biological catalysts known as the desaturases. The prototypical desaturase-mediated reaction is the "syn" 9,10-dehydrogenation of stearoyl CoA, which occurs in a wide variety of biological species and plays a pivotal role in the aerobic production of unsaturated lipids.[1] This process is catalyzed by

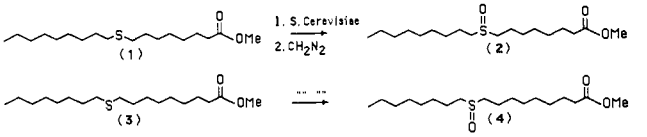


an O_2-dependent, non-heme iron protein which acquires its reducing equivalents from NAD(P)H via a NAD(P)H reductase and an intermediary electron-transfer protein such as cytochrome b_5. A topographical model, based on sequence information, has recently been constructed for the Δ^9-desaturases of rat liver and *Saccharomyces cerevisiae*.[2] However, precise information about

Scheme I



Scheme II



(1) Cook, H. In *Biochemistry of Lipids and Membranes*, Vance, D. E., Vance, J. E., Eds.; The Benjamin Cummings Publishing Co. Ltd.: Menlo Park, CA, 1985; pp 191–203.

0002-7863/92/1514-5073$03.00/0