Studies Dealing with the Excited-State Behavior of Substituted 8-Oxabicyclo[3.2.1]oct-6-en-2-ones†

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A series of 8-oxabicyclo[3.2.1]oct-6-en-2-ones was prepared by the rhodium(II)-catalyzed cyclization–cycloaddition reaction of α-diazopentanedione with various alkynes. The photochemical behavior of these oxabicyclic enones was investigated. Both direct and sensitized photolysis cleanly results in a 1,3-acyl shift. A slower, secondary photoprocess involving intramolecular hydrogen atom transfer and intramolecular cycloaddition of the resulting ketene was also uncovered. The photobehavior of the closely related 9-oxabenzocycloheptene system was also examined. The initially formed 1,3-sigmatropic rearranged product was found to undergo a novel 1,4-methoxyl migration on extended photolysis. The photochemistry of the homologous 7-oxabicyclo[2.2.1]hepten-2-one was studied. The results obtained can be interpreted in terms of an initial Norrish type I cleavage. The resulting diradical either couples to give the 1,3-acyl shift product or undergoes bond fragmentation, giving products derived from a stepwise retro-Diels–Alder reaction.

The diverse excited-state behavior exhibited by β,γ-unsaturated carbonyl compounds has attracted considerable attention over the past two decades and has been the subject of several reviews.[1-6] Much of the known photochemistry of β,γ-enones is dominated by 1,3-shifts occurring from excited singlet states and 1,2-shifts occurring from excited triplet states. A number of studies have shown that the former occurs from the n,π* singlet state whereas the oxadi-π-methane rearrangement proceeds from the triplet state which is primarily π,π* in character.[7-10] Evidence has also been obtained which demonstrates that, in certain cases, the 1,3-acyl shift is coupled not only with the singlet state but also from a higher lying T_2 state.[6] The intersystem crossing from the singlet to the triplet state, albeit inefficient, populates the T_2 (n,π*) state from which the 1,3-acyl shift occurs more readily than internal conversion to T_1.[11,12] In recent years the oxadi-π-methane reaction (ODPM) has been utilized by synthetic chemists for the preparation of natural products.[13-18] The ODPM rearrangement has been carried out with molecules containing unprotected functional groups as well as complex functionality patterns.[15] For synthetic purposes, the photoreaction of β,γ-unsaturated carbonyls is controllable by the use of appropriate triplet sensitizers and selection of the wavelength of excitation.

Our interest in the photochemistry of β,γ-enones originated from investigations in our laboratory dealing with the synthesis and chemistry of several 8-oxabicyclo-[3.2.1]oct-6-en-2-ones (1).[19] This bicyclic ring system contains a β,γ-unsaturated ketone as the active chromophore. Preliminary studies indicate that the 1,3-acyl shift (1 → 2) is indeed a facile photoinduced process.[20] The

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result of this rearrangement is the formation of a stereospecifically substituted 3a,6a-dihydrocyclopenta[b]furan-4-one (oxadiquinane) (2). A great deal of work has recently been focused on the synthesis of polyquinanes.[21] Much of this interest centers around the oxapolyquinanes; as natural product goals (e.g. ginkolides),[22] as oxa analogues to the naturally occurring carbocycles,[23] and as key intermediates in synthesis (particularly the prostaglandins, corrolins, and hirsutenes).[24-26] We have undertaken a more detailed investigation of the photochemistry of sev-

† Dedicated to Alfred Hassner on the occasion of his 60th birthday.

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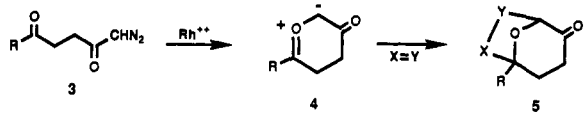
eral substituted 8-oxabicyclo[3.2.1]oct-6-en-2-ones with the hope of gaining an appreciation of the synthetic applicability of this reaction. The results reported below summarize various aspects of this effort.

Results and Discussion

Previous papers from these laboratories have described a route to oxapolycyclic ring systems which involves the tandem cyclization–cycloaddition reaction of a rhodium carbenoid derived from a α-diazoalkanedione.[19] The method consists of a rhodium(II)-induced diazo ketone cyclization onto a neighboring carbonyl group followed by 1,3-dipolar cycloaddition of the resulting cyclic carbonyl ylide. Several types of dipolarophiles were examined so



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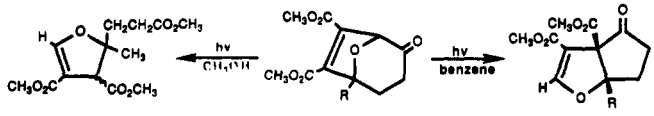
as to establish the scope and generality of the process. The cycloaddition proceeded readily with aldehydes, alkenes, and alkynes giving rise to excellent yields of dipolar cycloadducts of type **5**. The orientation observed with alkynes can readily be rationalized in terms of maximum overlap of the dipole HOMO–dipolarophile LUMO.[27] MNDO calculations on carbonyl ylide **4** clearly indicate that the largest coefficient in the HOMO resides on the enolate carbon.[28] This site becomes linked with the less substituted carbon atom of the alkyne.

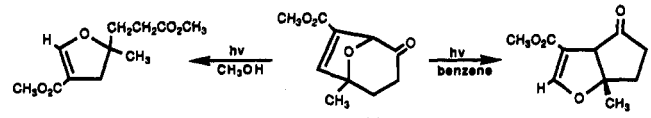
Each of the 8-oxabicyclo[3.2.1]oct-6-en-2-ones used in the photochemical study was prepared by the above route. Irradiation of a benzene solution of **6** for 2 h through Pyrex cleanly afforded 4*H*-cyclopenta[*b*]furan (**7**) in 90% yield. An analogous rearrangement occurred (95% yield) with the closely related phenyl-substituted system (i.e. **8**). The structures of the rearranged photoisomers were deduced on the basis of their spectral data (see the Experimental Section). These same products were also formed when



10 6; R=CH3 8; R=Ph 7; R=CH3 9; R=Ph

the photolysis was carried out in the presence of a triplet sensitizer (i.e. benzophenone or thioxanthone) or by using acetone as the solvent. In contrast to the results obtained in benzene, the direct irradiation of **6** in methanol was found to proceed differently in that the major product formed after 12 h corresponded to a 1:1 mixture of the diastereomers of 2,3-dihydro-2-methylfuran (**10**).

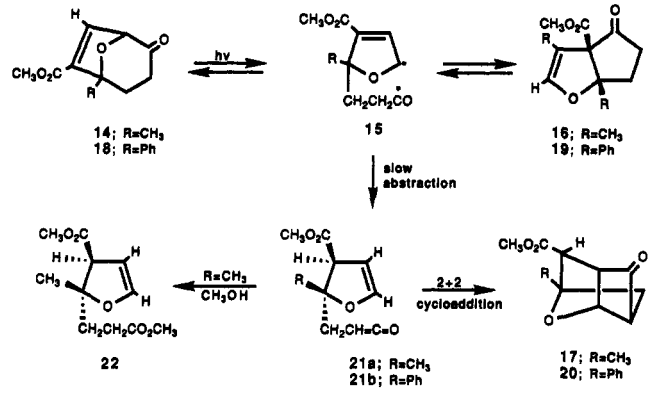
The photochemical behavior of keto ester **11** was also studied and was found to respond similarly to the change in solvent.[29] Irradiation of **11** in benzene for 2 h afforded the 1,3-sigmatropic rearranged isomer **12** whereas the photolysis in methanol for 12 h gave dihydrofuran **13** in good yield.[30]



13 11 12

Attention was next turned to the excited state behavior of the isomeric 6-carbomethoxy-substituted bicyclo[3.2.1]octenone **14**. In this case, the photolysis took a different course and cleanly afforded oxatricyclo[3.2.1.0^{3,7}]octanone **17** in 85% yield. The structure of this material was deduced on the basis of its spectral data (see the Experimental Section). Subsequent studies showed that **17** is not a primary reaction product but is formed by a subsequent photoreaction of a oxabicyclo[3.3.0]oct-3-en-6-one intermediate (i.e. **16**). With short exposures, oxabicyclooctenone **16** accounts for nearly all of the product produced. At longer exposures, owing to a secondary photoreaction of **16**, the amount of **17** substantially increased. This was independently demonstrated by the conversion of **16** to **17** under the photolytic conditions used. In a related manner, brief irradiation of enone **18** afforded the *cis*-fused bicycle **19** as the primary photoproduct. Once again, triplet sensitization provided similar results. When the direct irradiation was carried out for a total of 12 h, cyclobutanone **20** was isolated in 88% yield.

A reasonable mechanism to account for the formation of the oxatricyclo[3.2.1.0^{3,7}]octanone system involves a sequence consisting of Norrish type I cleavage of either enone **14** or **16** to give diradical **15** which subsequently undergoes an internal hydrogen transfer to produce a ketene intermediate (i.e. **21**). Intramolecular [2 + 2]-



14; R=CH3 18; R=Ph 15 16; R=CH3 19; R=Ph

22 21a; R=CH3 21b; R=Ph 17; R=CH3 20; R=Ph

cycloaddition of the cyclic enol ether with the reactive ketene explains the formation of the cyclobutanone. The conversion of **21** to **17** (or **20**) is a ground-state transformation which occurs with a relatively low energy barrier.[31] The isolation of dihydrofuran **22** provides strong support for the ketene intermediate. Apparently, the ketene prefers to add methanol across the C=C bond rather than give the more highly strained oxatricyclooctanone. This mechanism also provides a rationale for the formation of dihydrofurans **10** and **13** from the long-term photolysis of enones **6** and **11**.[30]

The stereospecific cycloaddition of ketenes to alkenes provides an attractive route to cyclobutanones and rep-

(26) Pentalenafurans in other studies: Pfenninger, A.; Roesle, A.; Keese, R. *Helv. Chim. Acta* **1985**, *68*, 493. Luyten, M.; Keese, R. *Helv. Chim. Acta* **1984**, *67*, 2242. Farnum, D. G.; Monego, T. *Tetrahedron Lett.* **1983**, *24*, 1361. Schori, H.; Patil, B. B.; Keese, R. *Tetrahedron* **1981**, *37*, 4457. Deslongchamps, P.; Cheriyan, H. O.; Lambert, Y.; Mercier, J. C.; Ruest, L.; Russo, R.; Soucy, P. *Can. J. Chem.* **1978**, *56*, 1687. Fritz, H.; Weiss, C. D.; Winkler, T. *Helv. Chim. Acta* **1975**, *58*, 1345. Cargill, R. L.; Foster, A. M.; Good, J. J.; Davis, F. K. *J. Org. Chem.* **1973**, *38*, 3829. Eicher, T.; Born, T. *Liebigs Ann. Chem.* **1972**, *762*, 127.

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(28) Calculations were performed with the Ampac program (QCPE 506) using the AM1 Hamiltonian.

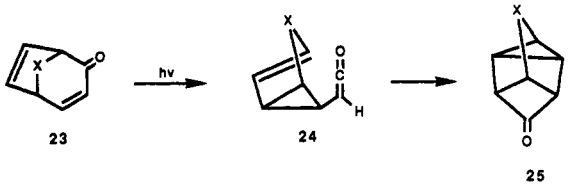
(29) Structure **11** corresponds to the minor product derived from the cycloaddition of 1-diazo-2,5-hexanedione with methyl propiolate.[50]

(30) The difference in product distribution as a function of solvent is probably related to the facility with which compounds **11** and **12** equilibrate upon irradiation. On extended photolysis, internal hydrogen transfer eventually occurs giving rise to a ketene intermediate which is rapidly trapped by methanol to give **13**.

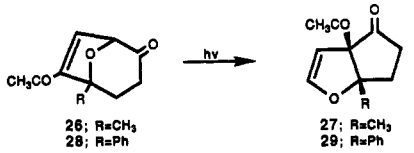
(31) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793. Snider, B. B.; Ron, E.; Burbaum, B. W. *J. Org. Chem.* **1987**, *52*, 5413.

resents one of the few general methods for carbofunctionalization of alkenes.[31] A number of research groups have come to recognize that the intramolecular version of the [2 + 2]-cycloaddition provides a general method for the synthesis of polycyclic cyclobutanones.[31-37] Although simple ketenes do react with some alkenes, satisfactory yields are not generally obtained unless activated ketenes are used. Extensive studies by Snider and his co-workers have demonstrated that electronic effects of substituents on the alkene rather than the connectivity pattern controls the regiochemistry of the internal cycloaddition.[38] Our inability to detect ketene **21** in the crude reaction mixture derived from the irradiation of **14** (or **18**) is probably related to the facility of the internal cycloaddition step. Groups such as oxygen which raise the energy of the HOMO of the alkene would be expected to enhance the [2 + 2]-cycloaddition rate. The regiospecificity of the cycloaddition is also controlled by electronic effects. The more nucleophilic β-carbon of the dihydrofuran adds to the carbonyl group of the ketene to produce cyclobutanone **17** (or **20**). Similar observations have been made by Snider in his studies dealing with the intramolecular [2 + 2]-reaction of ketenes using alkyl-substituted alkenes.

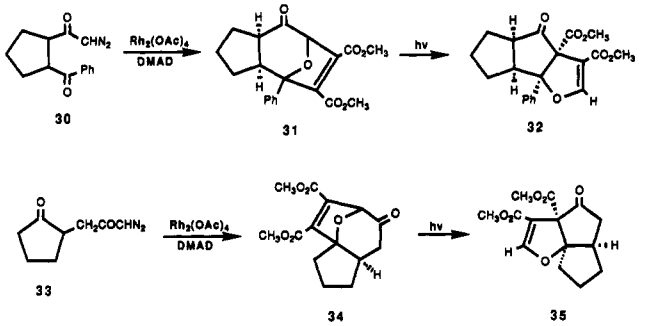
It should be pointed out that a somewhat related enone–ketene–cyclobutanone path has been previously described by Hart and co-workers.[40] Compounds of type **23** were shown to photoisomerize to ketenes (**24**), which, when completely substituted with methyl groups, undergo a facile intramolecular [2 + 2]-cycloaddition reaction to give cyclobutanone **25**.[41]



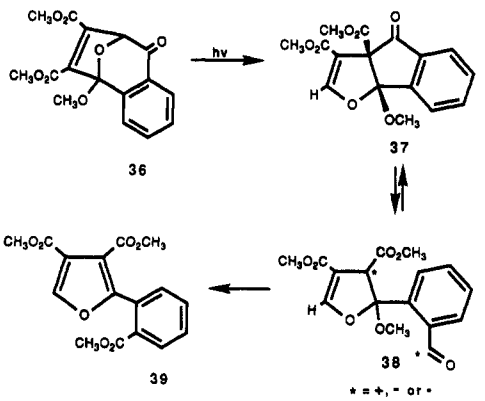
We have also examined the photochemical behavior of the acetyl-substituted 8-oxabicyclooctenones **26** and **28** in order to determine whether the mixed chromophore present in these enones would still allow the 1,3-sigmatropic reorganization to occur. In fact, both the direct and thioxanthone sensitized irradiation readily afforded the dihydrofuran in 90–95% yield.



Recent years have seen a number of elegant methods for the stereospecific preparation of triquinanes.[21] We felt that the combined rhodium(II)-catalyzed tandem cyclization–cycloaddition–photorearrangement methodology should provide a convenient access to the oxa analogues of these fascinating carbocycles. With this goal in mind, diazo dione **30** was prepared and allowed to undergo the rhodium-catalyzed cycloaddition with dimethyl acetylenedicarboxylate. Irradiation of the resulting cycloadduct **31** for 2 h cleanly afforded the linear oxatriquinane **32** in 79% yield. Encouraged with this success, the related diazo dione **33** was prepared and subjected to the usual conditions. Photolysis of the resulting cycloadduct **34** in benzene for 2 h cleanly afforded the bent oxatriquinane **35** in 96% yield. Note that in both **32** and **35**, adjacent quaternary centers are introduced efficiently and stereospecifically. These two examples establish the viability of this approach as a convenient and rapid entry into the oxatriquinanes.



During the course of our investigation, we found that the 9-oxabenzocycloheptene system (i.e. **36** and **40**) also exhibits some interesting photochemistry. Irradiation of **36** in benzene for 2 h results in a Norrish type I cleavage followed by radical recombination at the opposite allylic terminus to give the expected indenofuran **37** in 79% yield. However, when the photolysis of **36** was carried out for extended periods of time (8 h), a new and unexpected photoproduct (i.e. **39**) was obtained. This same material was also formed from the irradiation of indenofuran **37** in 90% yield. The formation of **39** is envisaged to involve a rather novel 1,4-methoxyl group migration from the diradical intermediate **38**. More than likely, the gain in aromaticity of the final product provides the driving force for this rare 1,4-migration.[42]



(32) DeMesmaeker, A.; Veenstra, S. J.; Ernest, B. *Tetrahedron Lett.* **1988**, *29*, 459.
(33) Marko, I.; Ronsamans, B.; Hesbain-Frisque, A.; Dumas, S.; Ghosez, L.; Ernest, B.; Greuter, H. *J. Am. Chem. Soc.* **1985**, *107*, 2192.
(34) Corey, E. J.; Kang, M.; Desai, M. C.; Ghosh, A. K.; Houpis, I. N. *J. Am. Chem. Soc.* **1988**, *110*, 649.
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(38) Snider, B. B.; Hui, R. A.; Kulkarni, Y. S. *J. Am. Chem. Soc.* **1985**, *50*, 2809. Kulkarni, Y. S.; Burbaum, B. W.; Snider, B. B. *Tetrahedron Lett.* **1985**, *26*, 5619. Snider, B. B.; Kulkarni, Y. S. *J. Org. Chem.* **1985**, *50*, 5167. Kulkarni, Y. S.; Niwa, M.; Ron, E.; Snider, B. B. *J. Org. Chem.* **1987**, *52*, 1568.
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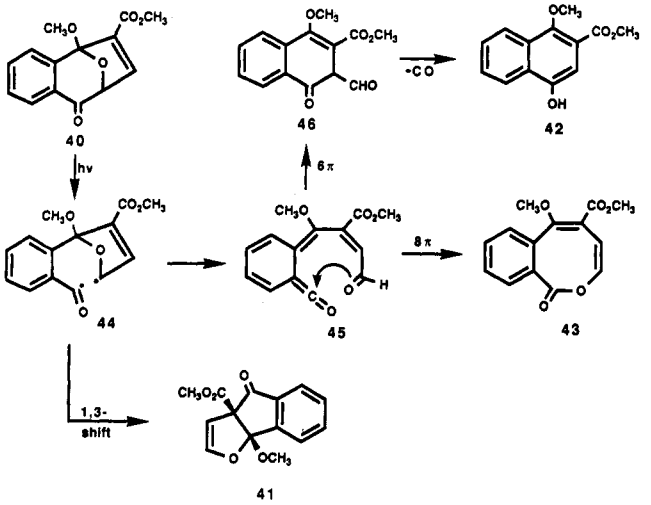
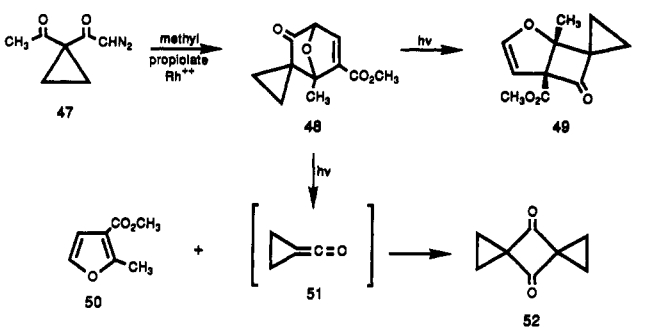
(40) Hart, H.; Love, G. M. *J. Am. Chem. Soc.* **1971**, *93*, 6266.
(41) See also Goldschmidt, Z.; Gutman, U.; Bakal, Y.; Worchel, A. *Tetrahedron Lett.* **1973**, 3759.
(42) For some examples of 1,4-group migrations, see: Abdun-Nur, A. R.; Bordwell, F. G. *J. Am. Chem. Soc.* **1964**, *86*, 5695. Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 5143. Rucker, C. *Tetrahedron Lett.* **1984**, *25*, 4349. Mora, A.; Costa, A. *Tetrahedron Lett.* **1984**, *25*, 3493. Bures, E. J.; Keay, B. A. *Tetrahedron Lett.* **1987**, *28*, 5965. Spinazze, P. G.; Keay, B. A. *Tetrahedron Lett.* **1989**, *30*, 1765. Coqueret, X.; Bourelle-Wargnier, F.; Chuche, J.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1983**, 1144.

It is interesting to note that the closely related 5*H*-benzocycloheptene **40** followed a slightly different path. In this case, the photolysis afforded a mixture of three products which were identified as indeno[1,2-*b*]furan **41** (50%), naphthol **42** (20%), and benzoxocin **43** (20%). The major product is the result of a 1,3-acyl shift. The formation of the two minor products is explicable in terms of a photoinduced Norrish type I ring cleavage of **40** to give diradical **44**. In addition to recombination of the radical centers, the diradical can also undergo ring fragmentation to give ketene **45**. This reactive species has the appropriate structural elements to undergo a rapid 6π- or 8π-electrocyclization. The 8π-cyclization route leads to benzoxocin **43** whereas the 6π-closure affords **46** as a transient intermediate. More than likely this material undergoes ready deformylation under the reaction conditions to give naphthol **42**.



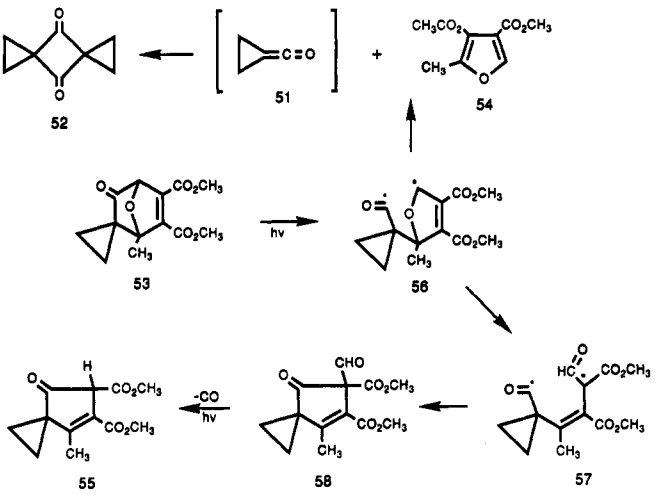
The quantum efficiency of β,γ-enone photochemistry is known to be strongly coupled with the degree of flexibility of the C=C bond[2,3] and consequently, the conformationally rigid [2.2.1] bridged skeleton has been examined in some detail. Direct irradiation of the parent 2-norbornenone affords the 1,3-shift isomer,[43] whereas triplet sensitization gives mainly the 1,2-acyl shift product.[44] As part of our own investigations in this area, we decided to examine the photobehavior of the homologous 7-oxabicyclo[2.2.1]hepten-2-one system (i.e. **48** and **53**). These materials were readily prepared by treating α-diazo ketone **47** with a catalytic amount of rhodium(II) acetate in benzene with an activated alkyne as the trapping agent.[45] Direct irradiation of **48** in benzene with Pyrex-filtered light afforded a mixture of three compounds. These structures were assigned a spirodihydrofuran **49** (45%), furan **50** (50%), and dispirooctanedione **52**.

The photochemistry can be rationalized in terms of a Norrish type I cleavage of enone **48**. The resulting diradical can either couple to give **49** or fragment to produce furan **50** and cyclopropylidene ketene **51**. Dione **52** is presumably formed by dimerization of **51** at 0 °C. Ketene **51** is a highly reactive species that has previously been generated by Brown and his co-workers when they submitted a spiroannulated Meldrum acid to flash vapor thermolysis (500 °C).[46] Cyclopropylidene ketene **51** has been suggested not to be linear, but marginally bent away

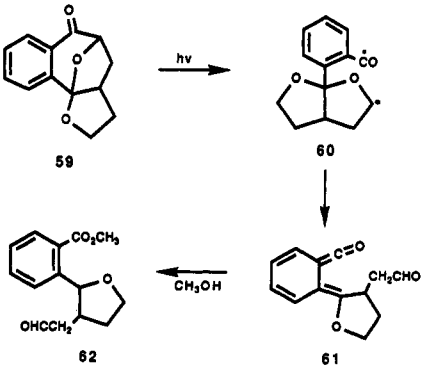


from the symmetrical conformer.[47] It was found to dimerize to dispirodione **52** below 0 °C.

We have also studied the photobehavior of the closely related oxabicyclic **53**. In this case, the photolysis afforded a mixture of furan **54** (65%), spirocyclopentenone **55** (30%), and the spirodione **52**. While the formation of **54** is straightforward, the production of **55** represents a more complicated process. The reaction may be pictured as



proceeding by acyl bond cleavage to give diradical **56**. This reactive species then undergoes fragmentation of the C–O bond to generate a new diradical **57**. Coupling of the radical centers followed by a subsequent deformylation explains the observed product.[48] It should be noted that the fragmentation reaction is analogous to a path previously suggested to account for the photobehavior of benzo[6,7]cyclohepta[1,2-*b*]furanone (**59**).[49]



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(47) Brown, R. F. C. *Chem. Br.* **1987**, 1189; **1988**, 770.
(48) In this case, we were not able to separate the small amount of oxabicyclo[3.2.0]heptenone that was present in the crude reaction mixture. Presumably this material is converted to diradical **56** under the irradiation conditions.
(49) Padwa, A.; Carter, S. P.; Nimmesgern, H.; Stull, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 2894.

One final point has to do with the multiplicity effects observed with these enones. We have found that the triplet sensitized irradiation of the oxabicyclo[3.2.1]octenone system does not lead to an oxadi-π-methane rearrangement. Instead, the products formed are derived from an α-cleavage reaction. There are a number of reports in the literature where related observations have been made.[11] The accumulated evidence suggests that, in certain cases, the T_2 states of β,γ-enones can be reactive in competition with decay to the T_1 state. Although we have no hard evidence, it seems reasonable to assume that the T_2 $(n\text{-}\pi^*)^3$ state is responsible for the 1,3-shifts encountered on triplet sensitization.

In conclusion, we have established that the direct or sensitized photoexcitation of 8-oxabicyclo[3.2.1]oct-6-en-2-ones cleanly results in a 1,3-acyl shift. The rhodium-catalyzed tandem cyclization–cycloaddition–photorearrangement sequence provides rapid, stereospecific access to a variety of oxapolyquinanes. A slower, secondary photoprocess involving intramolecular hydrogen atom transfer and intramolecular cycloaddition of the resulting ketene was also discovered. We are continuing to explore the scope of this tandem methodolgy and will report additional findings at a later date.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Starting material for all irradiations were prepared from the rhodium(II)-catalyzed reaction of the appropriate diazo ketone with various alkynes.[50]

General Procedure for Photolysis of Cycloadducts. UV irradiations were carried out using a 450-W (type 679A36) Hanovia medium-pressure mercury arc lamp centered in an internal water-cooled quartz immersion well with the appropriate filter sleeve. Reaction mixtures were purged with dry argon prior to irradiation, and a positive pressure of argon was maintained throughout the irradiation. The solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel chromatotron plate using an ethyl acetate–hexane mixture as the eluent.

Photochemical Rearrangement of Dimethyl 5-Methyl-2-oxo-8-oxabicyclo[3.2.1]oct-6-ene-6,7-dicarboxylate (6). Irradiation of a 0.05 M benzene solution of keto ester **6** for 2 h using a Pyrex filter sleeve resulted in the formation of 89 mg of dimethyl 6a-methyl-4-oxa-3a,5,6,6a-tetrahydro-4*H*-cyclopenta[*b*]furan-3,3a-dicarboxylate (**7**) as a colorless oil in 90% yield: IR (neat) 1768, 1750, 1720, 1620, 1255, and 1150 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 3 H), 2.12 (ddd, 1 H, J = 13.5, 12.0, and 8.6 Hz), 2.35–2.52 (m, 2 H), 2.58 (ddd, 1 H, J = 17.6, 12.0, and 8.8 Hz), 3.70 (s, 3 H), 3.75 (s, 3 H), and 7.36 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.5, 34.6, 36.0, 51.4, 52.7, 69.3, 100.8, 108.4, 159.2, 163.2, 167.8, and 206.7; UV (acetonitrile) 252 (ϵ 7700) and 304 nm (ϵ 490); MS m/e 254, 222, 194, 167, 166, 162, 135, 123, and 99; HRMS calcd for $C_{12}H_{14}O_6$ 254.0790, found 254.0779.

Irradiation of 230 mg of keto ester **6** in methanol for 12 h through Pyrex afforded a 1:1 mixture of the diastereomers of methyl 3,4-dicarbomethoxy-2,3-dihydro-2-methylfuran-2-propanoate (**10**) in 56% yield which could be separated by silica gel chromatography. One of the diastereomers showed the following spectral properties: IR (neat) 1740, 1710, 1630, and 1440 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.43 (s, 3 H), 2.03–2.18 (m, 2 H), 2.38–2.48 (m, 2 H), 3.66 (s, 3 H), 3.68 (s, 3 H), 3.70 (s, 1 H), 3.71 (s, 3 H), and 7.25 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 28.2, 31.1, 36.8, 51.2, 51.8, 54.9, 92.1, 108.2, 157.1, 164.6, 170.6, and 173.0; HRMS calcd for $C_{13}H_{18}O_7$ 286.1052, found 286.1040.

The other diastereomer showed the following properties: IR (neat) 1740, 1710, 1630, and 1440 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 3 H), 1.92 (dt, 1 H, J = 14.6 and 7.3 Hz), 2.03–2.18 (m, 1 H), 2.38–2.48 (m, 2 H), 3.65 (s, 3 H), 3.68 (s, 3 H), 3.69 (s, 1 H), 3.72 (s, 3 H), and 7.25 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 26.2, 28.7, 32.8, 52.1, 52.2, 56.8, 92.2, 108.4, 157.0, 164.7, 170.6, and 173.2; HRMS calcd for $C_{13}H_{18}O_7$ 286.1052, found 286.1040.

Dimethyl 4-Oxa-6a-phenyl-3a,5,6,6a-tetrahydro-4*H*-cyclopenta[b]furan-3,3a-dicarboxylate (9). Irradiation of a 0.05 M benzene solution of dimethyl 2-oxo-5-phenyl-8-oxabicyclo[3.2.1]oct-6-ene-6,7-dicarboxylate (**8**) for 2 h using a Pyrex filter sleeve produced 88 mg of the 1,3-sigmatropic rearrangement product **9** in 95% yield: IR (neat) 1750, 1630, 1270, 1160, 770, and 710 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.50–2.60 (m, 1 H), 2.65–2.90 (m, 3 H), 3.13 (s, 3 H), 3.66 (s, 3 H), 7.21–7.38 (m, 5 H), and 7.66 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.7, 36.1, 51.4, 52.1, 71.7, 103.1, 125.2, 128.2, 128.8, 137.1, 159.5, 159.6, 162.9, 166.8, and 205.6 ppm; HRMS calcd for $C_{17}H_{16}O_6$ 316.0947, found 316.0959.

Photochemical Rearrangement of Methyl 5-Methyl-2-oxo-8-oxabicyclo[3.2.1]oct-6-ene-7-carboxylate (11). Irradiation of a 0.05 M benzene solution of keto ester **11** for 2 h using a Pyrex filter sleeve afforded 60 mg of a single product (90% yield) whose structure was assigned as methyl 6a-methyl-4-oxa-3a,5,6,6a-tetrahydro-4*H*-cyclopenta[*b*]furan-3-carboxylate (**12**): IR (neat) 1760, 1715, 1620, 1260, 1165, and 770 cm^{-1}; NMR (300 MHz, $CDCl_3$ δ 1.48 (s, 3 H), 1.95–2.06 (m, 1 H), 2.25–2.48 (m, 2 H), 2.53 (ddd, 1 H, J = 16.5, 12.3, and 8.5 Hz), 3.22 (s, 1 H), 3.68 (s, 3 H), and 7.25 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0, 34.5, 36.3, 51.2, 57.3, 98.1, 107.3, 157.7, 164.3, and 212.1; UV (methanol) 254 (ϵ 7070) and 300 nm (ϵ 360); MS m/e 196, 165, 153, 136, 123, and 109; HRMS calcd for $C_{10}H_{12}O_4$ 196.0735, found 196.0745.

Irradiation of 200 mg of **11** (or **12**) in 40 mL of methanol for 12 h using a Pyrex filter sleeve afforded 112 mg of methyl 4-carbomethoxy-2,3-dihydro-2-methylfuran-2-propanoate (**13**) (65% yield): IR (neat) 1740, 1705, 1625, 1440, 1285, and 1085 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 3 H), 1.99 (t, 2 H, J = 8.0 Hz), 2.38 (t, 2 H, J = 8.0 Hz), 2.56 (d, 1 H, J = 14.7 Hz), 2.66 (d, 1 H, J = 14.7 Hz), 3.66 (s, 3 H), 3.68 (s, 3 H), and 7.12 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.4, 28.7, 35.8, 38.9, 51.0, 51.7, 91.0, 107.6, 155.6, 165.6, and 173.5; MS m/e 228, 196, 169, 165, 164, 155, 141, 137, 136, 127, 122, and 99; HRMS calcd for $C_{11}H_{16}O_5$ 228.0998, found 228.0993.

Photochemical Rearrangement of Methyl 5-Methyl-2-oxo-8-oxabicyclo[3.2.1]oct-6-ene-6-carboxylate (14). Irradiation of a 0.05 M acetone solution of keto ester **14** (100 mg) for 2 h through a Pyrex filter sleeve afforded 65 mg of methyl 6a-methyl-4-oxa-3a,5,6,6a-tetrahydro-4*H*-cyclopenta[*b*]furan-3a-carboxylate (**16**) in 75% yield; IR (neat) 1765, 1725, 1620, 1270, 1115, and 735 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 3 H), 2.13 (ddd, 1 H, J = 13.8, 12.0, and 8.4 Hz), 2.30–2.46 (m, 2 H), 2.58 (ddd, 1 H, J = 17.8, 12.0, and 8.8 Hz), 3.70 (s, 3 H), 4.95 (d, 1 H, J = 2.6 Hz), and 6.42 (d, 1 H, J = 2.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 35.1, 36.1, 52.5, 72.0, 95.8, 99.4, 148.8, 169.3, and 210.6; UV (methanol) 230 (ϵ 2600) and 302 nm (ϵ 540); MS m/e 196, 165, 153, 137, 109, and 99; HRMS calcd for $C_{10}H_{12}O_4$ 196.0735, found 196.0729.

When the irradiation of a 0.05 M benzene solution of **14** (200 mg) was carried out for 15 h, a single product was isolated in 85% yield whose structure was assigned as methyl 5-methyl-2-oxo-6-oxatricyclo[3.2.1.0^{3,7}]octane-4-carboxylate (**17**) on the basis of its spectral data: IR (neat) 1785, 1745, 1445, 1270, and 850 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 3 H), 1.97 (dd, 1 H, J = 12.5 and 9.6 Hz), 2.20 (d, 1 H, J = 12.5 Hz), 3.02 (s, 1 H), 3.18 (ddd, 1 H, J = 9.6, 8.2, and 3.4 Hz), 3.41 (dd, 1 H, J = 8.2 and 3.4 Hz), 3.66 (s, 3 H), and 5.01 (t, 1 H), J = 3.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.9, 46.1, 52.1, 57.3, 60.8, 63.3, 69.8, 84.6, 169.7, and 202.7; MS m/e 196, 181, 165, 153, 125, and 99; HRMS calcd for $C_{10}H_{12}O_4$ 196.0735, found 196.0732.

This same material was isolated in high yield by carrying out the irradiation of 100 mg of **16** in benzene for 15 h. Irradiation of a methanol solution of **14** (300 mg) for 10 h through Pyrex afforded a 1:2 mixture of the diastereomers of methyl 3-carbomethoxy-2,3-dihydro-2-methylfuran-2-propanoate (**22**) in 63% yield. One of the diastereomers exhibited the following spectral properties: IR (neat) 1745 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 3 H), 1.75 (ddd, 1 H, J = 14.2, 9.2, and 6.7 Hz), 1.98–2.08 (m, 1 H), 2.35–2.44 (m, 2 H), 3.53 (m, 1 H), 4.85 (t, 1 H, J = 2.4 Hz), and 6.29 (t, 1 H, J = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 28.8, 30.7, 51.5, 51.8, 57.9, 87.2, 98.7, 146.4, 172.1, and 173.6. The second isomer showed the following spectral properties: IR (neat)

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1745 cm^{-1}; NMR (300 MHz), $CDCl_3$) δ 1.19 (s, 3 H), 1.98–2.08 (m, 2 H), 2.35–2.44 (m, 2 H), 3.53 (t, 1 H), J = 2.3 Hz), 4.80 (t, 1 H, J = 2.3 Hz), and 6.29 (t, 1 H, J = 2.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 28.6, 36.6, 51.6, 51.8, 56.0, 87.3, 98.3, 146.7, 172.2, and 173.5.

Photochemical Rearrangement of Methyl 5-Phenyl-2-oxo-8-oxabicyclo[3.2.1]oct-6-ene-6-carboxylate (18). Irradiation of a 0.05 M benzene solution containing keto ester 18 was carried out for 12 h using a Pyrex filter sleeve. The solvent was removed under reduced pressure, and the residue was crystallized from either to give 80 mg (88% yield) of methyl 5-phenyl-2-oxo-6-oxatricyclo[3.2.1.0^{3,7}]octane-4-carboxylate (**20**) as a white solid: mp 156–157 °C; IR (KBr) 1785, 1735, 1370, 1227, 1210, and 705 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.21 (dd, 1 H, J = 12.6 and 9.6 Hz), 2.75 (d, 1 H, J = 12.6 Hz), 3.27 (s, 3 H), 3.37 (ddd, 1 H, J = 9.6, 8.2, and 3.5 Hz), 3.45 (s, 1 H), 3.59 (dd, 1 H, J = 8.2 and 3.5 Hz), 5.30 (t, 1 H, J = 3.5 Hz), and 7.32–7.48 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.8, 51.6, 58.8, 60.8, 63.8, 69.6, 88.7, 125.3, 128.1, 128.2, 134.9, 169.0, and 202.5; HRMS calcd for $C_{15}H_{14}O_4$ 258.0892, found 258.0891.

If the irradiation of 18 was carried out for only 2 h, 50 mg of the 1,3-sigmatropic shift product, methyl 4-oxa-6a-phenyl-3a,5,6,6a-tetrahydro-4*H*-cyclopenta[*b*]furan-3a-carboxylate (**19**) was isolated in 70% yield: IR (neat) 1755, 1740, 1270, 1165, 755, and 705 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.53–2.84 (m, 3 H), 2.93 (ddd, 1 H, J = 15.2, 10.8, and 7.3 Hz), 3.23 (s, 3 H), 5.11 (d, 1 H), J = 2.6 Hz), 6.75 (d, 1 H, J = 2.6 Hz), and 7.28–7.48 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.2, 36.0, 51.9, 74.4, 98.1, 100.0, 125.4, 128.1, 128.5, 138.3, 150.0, 168.3, and 209.3; HRMS calcd for $C_{15}H_{14}O_4$ 258.0892, found 258.0887.

Photochemical Rearrangement of 6-Acetyl-5-methyl-8-oxabicyclo[3.2.1]oct-6-ene-2-one (26). Irradiation of a 0.05 M benzene solution of keto ester **26** for 2 h through Pyrex afforded 100 mg of 3a-acetyl-6a-methyl-4-oxa-3a,5,6,6a-tetrahydro-4*H*-cyclopenta[*b*]furan (**27**) in 90% yield as a colorless oil: IR (neat) 1750, 1705, 1605, 1365, 1240, 1170, and 1065 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 3 H), 2.06–2.21 (m, 1 H), 2.25 (s, 3 H), 2.34–2.48 (m, 2 H), 2.59 (ddd, 1 H, J = 17.6, 10.5, and 4.0 Hz), 5.07 (d, 1 H, J = 2.6 Hz), and 6.55 (d, 1 H, J = 2.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 30.6, 35.3, 35.4, 36.4, 96.1, 99.9, 149.3, 206.5, and 212.7; MS m/e 180, 138, 137, 125, 109, 99, and 95; HRMS calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0794.

Photochemical Rearrangement of 6-Acetyl-5-phenyl-8-oxabicyclo[3.2.1]oct-6-ene-2-one (28). Irradiation of a 0.05 M benzene solution of keto ester **28** for 2 h through Pyrex filter afforded 88 mg (95% yield) of a major product whose structure was assigned as 3a-acetyl-4-oxa-6a-phenyl-3a,5,6,6a-tetrahydro-4*H*-cyclopenta[*b*]furan (**29**): IR (neat) 1750, 1705, 1615, 1165, 760, and 710 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.57 (s, 3 H) 2.53–2.90 (m, 4 H), 5.12 (d, 1 H, J = 2.7 Hz), 6.80 (d, 1 H, J = 2.7 Hz), and 7.3–7.4 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.5, 34.3, 36.3, 79.4, 98.5, 100.7, 125.7, 128.2, 128.5, 138.2, 150.2, 205.4, and 211.7; MS m/e 242, 213, 187, 171, 157, 129, 115, 105, 91 and 77; HRMS calcd for $C_{15}H_{14}O_3$ 242.0943, found 242.0934.

Photochemical Rearrangement of Dimethyl 1,2,3,3a,4,7,8,8a-Octahydro-8-oxa-4-phenyl-4,7-epoxyazulene-5,6-dicarboxylate (31). Irradiation of a 0.05 M benzene solution containing of keto ester **31**[51] for 2 h through a Pyrex filter sleeve resulted in the formation of 150 mg (79% yield) of dimethyl 3a,3b,4,5,6,6a,7,7a-octahydro-3a-phenyl-7-oxopentaleno[1,2-*b*]-furan-1,7a-dicarboxylate (**32**), which could be isolated as a crystalline solid: mp 134–135 °C; IR (KBr) 1765, 1725, 1705, 1620, 770, and 710 cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.5, 27.6, 28.9, 51.4, 52.2, 52.9, 55.3, 73.9, 100.8, 109.7, 125.2, 128.1, 139.9, 157.8, 163.2, 167.7, and 210.8; NMR ($CDCl_3$, 300 MHz) δ 1.45–1.69 (m, 3 H), 1.83–2.18 (m, 3 H), 3.10 (s, 3 H), 3.24–3.50 (m, 2 H), 3.71 (s, 3 H), 7.23–7.40 (m, 5 H), and 7.53 (s, 1 H). Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.47; H, 5.67.

Photochemical Rearrangement of Dimethyl 2,3,6,7,8,8a-Hexahydro-7-oxa-1*H*-3a,6-epoxyazulene-4,5-dicarboxylate (34). A solution containing 180 mg of cycloadduct **34**[50] in 35 mL of acetonitrile was degassed with argon and irradiated for 2 h using a Pyrex filter sleeve. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel plate using a 3:1 hexane–ethyl acetate mixture as the eluent to give 173 mg (96% yield) of the rearranged dimethyl 3a,4,5a,6,7,8-hexahydro-4-oxa-5*H*-pentaleno[6a,1-*b*]furan-3,3a-dicarboxylate (**35**): mp 104–105 °C; IR (KBr) 1770, 1735, 1715, 1615, 770, and 730 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.39–1.54 (m, 1H), 1.56–1.73 (m, 1 H), 1.88–2.17 (m, 5 H), 2.18–2.36 (m, 2 H), 2.54 (dd, 1 H, J = 13.7 and 4.1 Hz), 3.72 (s, 3 H), 3.75 (s, 3 H), and 7.35 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.0, 23.2, 30.6, 38.4, 47.9, 51.4, 52.8, 66.2, 109.6, 112.0, 158.4, 163.0, 167.2, and 207.1; HRMS calcd for $C_{14}H_{16}O_6$ 280.0947, found 280.0941.

Photochemical Rearrangement of Dimethyl 8,9-Dihydro-5-methoxy-9-oxa-5,8-epoxy-5*H*-benzocycloheptene-6,7-dicarboxylate (36). A sample of keto ester **36** was obtained in 90% yield from the reaction of *o*-carbomethoxy-α-diazoacetophenone[52] and dimethyl acetylenedicarboxylate in the prescence of rhodium(II) acetate as catalyst according to the method of Ibata:[53] NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3 H), 3.83 (s, 3 H), 3.84 (s, 3 H), 5.48 (s, 1 H), and 7.50–8.00 (m, 4 H); UV (methanol) 236 (ϵ 12 200), 295 (ϵ 1300), and 360 nm (ϵ 170). Irradiation of a 0.05 M benzene solution of **36** for 2 h using a Pyrex filter was followed by concentration of the solution under reduced pressure. The crude photolysate was chromatographed on silica gel, and the major fraction isolated contained 75 mg of a white solid (79% yield) which was identified as dimethyl 3a,8b-dihydro-8b-methoxy-4-oxa-4*H*-indeno[1,2-*b*]furan-3,3a-dicarboxylate (**37**): mp 154–155 °C; IR (KBr) 1760, 1735, 1620, 1275, 1250, and 800 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 3.62 (s, 3 H), 3.78 (s, 3 H), 3.79 (s, 3 H), 7.42 (s, 1 H), and 7.61–7.95 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.5, 53.1, 53.5, 109.7, 118.6, 124.8, 124.9, 131.6, 135.9, 136.1, 147.4, 158.6, 162.7, 166.7, and 193.1; UV (methanol) 240 (ϵ 19 000), 280 (ϵ 1500), and 340 nm (ϵ 250). Anal. Calcd for $C_{16}H_{14}O_7$: C, 60.40; H, 4.40. Found: C, 60.32; H, 4.44.

When the photolysis of **36** was carried out for 8 h or when **37** was irradiated for 6 h in benzene through a Pyrex filter, the major material isolated (85 mg, 90% yield) was identified as dimethyl 2-(2-carbomethoxyphenyl)furan-3,4-dicarboxylate (**39**): IR (neat) 1725, 1550, 1480, 1290, 765, and 720 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 3.71 (s, 3 H), 3.76 (s, 3 H), 3.86 (s, 3 H), 7.50–7.62 (m, 3 H), and 7.96–8.02 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.9, 52.0, 52.4, 114.4, 119.2, 129.2, 129.9, 130.3, 131.1, 131.4, 131.5, 146.7, 156.5, 162.2, 163.0, and 166.8; MS m/e 318, 287, 259, 228, 197, 163, 157, 132, and 104; HRMS calcd for $C_{16}H_{14}O_7$ 318.0739, found 318.0734.

Photochemical Rearrangement of Methyl 8,9-Dihydro-5-methoxy-9-oxa-5,8-epoxy-5*H*-benzocycloheptene-6-carboxylate (40). Structure **40** was obtained in 80% yield as a colorless oil from the reaction of *o*-carbomethoxy-α-diazoacetophenone and methyl propiolate according to the method of Ibata:[53] NMR (300 MHz, $CDCl_3$) δ 3.52 (s, 3 H), 3.69 (s, 3 H), 5.18 (d, 1 H, J = 2.4 Hz), 7.26 (d, 1 H, J = 2.4 Hz), 7.37 (t, 1 H, J = 7.4 Hz), 7.47 (t, 1 H, J = 7.4 Hz), 7.55 (d, 1 H, J = 7.4 Hz), and 7.77 (d, 1 H, J = 7.4 Hz); UV (methanol) 238 (ϵ 5800), 274 (ϵ 3200), and 360 nm (ϵ 220). Irradiation of a 0.05 M benzene solution of **40** (260 mg) for 4 h using a Pyrex filter sleeve produced a mixture of three products which could be separated by silica gel chromatography. The major component (120 mg) was identified as methyl 3a,8b-dihydro-8b-methoxy-4-oxa-4*H*-indeno-[1,2-*b*]furan-3a-carboxylate (**41**) (50%) on the basis of its spectral properties: IR (neat) 1750, 1725, 1610, 1280, 770, and 740 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 3.50 (s, 3 H), 3.75 (s, 3 H), 5.40 (d, 1 H, J = 3.0 Hz), 6.52 (d, 1 H, J = 3.0 Hz), 7.58 (t, 1 H, J = 7.4 Hz), 7.77 (t, 1 H, J = 7.4 Hz), and 7.85 (t, 2 H, J = 7.77 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.5, 52.8, 70.1, 101.5, 114.8, 124.3, 124.6, 130.8, 135.1, 135.9, 146.8, 150.0, 168.2, and 196.0; UV (methanol) 244 (ϵ 10 700), 284 (ϵ 1800), and 340 nm (ϵ 500); MS m/e 260, 229, 217, 201, 173, 163, 157, 143, 129, 115, 102, and 101; HRMS calcd for $C_{14}H_{12}O_5$ 260.0684, found 260.0694.

The second component isolated from the silica gel plate (48 mg) was assigned as methyl 4-hydroxy-1-methoxynaphthalene-2-carboxylate (**42**) (20%): mp 131–132 °C; IR (KBr) 1660, 1640, 1605, 1395, 1360, 1255, and 775 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 3.92 (s, 3 H), 3.95 (s, 3 H), 6.95 (s, 1 H), 7.53 (dd, 1 H, J = 8.1 and 6.8 Hz), 7.60 (dd, 1 H, J = 8.1 and 6.8 Hz), 8.16 (d, 1 H, J

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= 8.1 Hz), 8.36 (d, 1 H, J = 8.1 Hz), and 11.59 (s, 1 H exchanged with D_2O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 55.6, 100.2, 104.2, 121.9, 123.7, 125.5, 126.4, 128.9, 129.8, 147.6, 155.6, and 171.3; MS m/e 232, 200, 129, 102, and 101. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.27; H, 5.22.

The last component isolated from the silica gel plate (45 mg) was assigned as methyl 5-methoxy-2-oxo-3-benzoxocine-6-carboxylate (**43**) (20%): mp 120–121 °C; IR (KBr) 1765, 1720, 1620, 1240, 805, and 785 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 3.56 (s, 3 H), 3.79 (s, 3 H), 5.89 (d, 1 H, J = 6.3 Hz), 6.37 (d, 1 H, J = 6.3 Hz), 7.33–7.38 (m, 1 H), and 7.47–7.60 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.7, 59.2, 107.0, 117.7, 126.8, 127.3, 130.4, 131.1, 132.2, 140.1, 161.8, 164.5, and 168.2; MS m/e 260, 231, 229, 217, 201 (base), 157, and 101; HRMS calcd for $C_{14}H_{12}O_5$ 260.0684, found 260.0676.

Photochemical Rearrangement of Spiro[5-carbomethoxy-4-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-one-3,1′-cyclopropane] (48). Irradiation of a 0.05 M solution of spirocyclopropane **48**[45] (210 mg) in benzene through a Pyrex filter sleeve for 1 h gave rise to a mixture of three products. Chromatography of the mixture on a silica gel column using an ethyl acetate–hexane mixture as the eluent afforded 52 mg (45% yield) of spiro[5-carbomethoxy-1-methyl-2-oxabicyclo[3.2.0]hept-3-en-6-one-7,1′-cyclopropane] (**49**): NMR (300 MHz, $CDCl_3$) δ 1.31–1.55 (m, 4 H), 1.55 (s, 3 H), 3.79 (s, 3 H), 5.17 (d, 1 H, J = 2.8 Hz), and 6.57 (d, 1 H, J = 2.8 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.7, 16.2, 16.9, 48.5, 52.3, 87.4, 99.9, 141.3, 149.4, 166.9, and 203.7. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.27; H, 5.62.

One of the two other minor photoproducts was identified on the basis of its spectral properties as dispiro[2.1.2.1]octane-4,8-dione (**52**)[54] (50%): mp 180–181 °C; IR (KBr) 1740, 1350, 1080, 1020, and 790 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.94 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 50.5, and 209.6; HRMS calcd for $C_8H_8O_2$ 136.0524, found 136.0524.

The other compound (71 mg) was assigned as methyl 2-methylfuran-3-carboxylate (**50**) (50%): NMR (300 MHz, $CDCl_3$) δ 2.57 (s, 3 H), 3.82 (s, 3 H), 6.63 (d, 1 H, J = 1.9 Hz), and 7.22 (d, 1 H, J = 1.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, 51.1, 110.5, 113.1, 140.2, 159.2, and 164.4. Anal. Calcd for $C_7H_8O_3$: C, 59.98; H, 5.76. Found: C, 59.97; H, 5.62.

Photochemical Rearrangement of Spiro[5,6-dicarbomethoxy-4-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-one-3,1′-cyclopropane] (53). Photolysis of a 0.05 M solution of spirocyclopropane **53**[45] (270 mg) in benzene for 2 h using a Pyrex filter sleeve afforded a mixture of three products which were separated by silica gel chromatography. The first fraction isolated from the column contained 110 mg (65%) and was assigned as dimethyl 2-methylfuran-3,4-dicarboxylate (**54**): IR (neat) 1735, 1450, 1310, 1210, 1095, and 1040 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.51 (s, 3 H), 3.83 (s, 3 H), 3.86 (s, 3 H), and 7.75 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 51.7, 51.8, 112.7, 118.6, 145.4, 159.2, 162.4, and 163.4. Anal. Calcd for $C_9H_{10}O_5$: C, 54.55; H, 5.09. Found: C, 54.37; H, 5.02.

The second component isolated from the column was assigned as dispiro[2.1.2.1]octane-4,8-dione (**52**)[54] by comparison of its spectral properties with a sample obtained from the photolysis of **48**. The last material isolated from the column was assigned as dimethyl 7-methyl-2-oxospiro[2.4]hept-6-ene-5,6-dicarboxylate (**55**) (30%): IR (neat) 1765, 1735, 1370, 1225, 1160, and 1100 cm^{-1}, NMR (300 MHz, $CDCl_3$) δ 4.27 (q, 1 H, J = 1.7 Hz), 3.76 (s, 6 H), 2.04 (d, 3 H, J = 1.7 Hz), and 1.35–1.57 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.6, 18.0, 18.6, 40.1, 51.4, 52.7, 59.3, 122.3, 157.5, 163.7, 167.4, and 206.9. Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.39; H, 5.78.

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Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra (75 MHz) for all compounds with high-resolution mass spectra (18 pages). Ordering information is given on any current masthead page.

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Enantioselective Formation of Functionalized 1,3-Disubstituted Allenes: Synthesis of α-Allenic ω-Carbomethoxy Alcohols of High Optical Purity[1]

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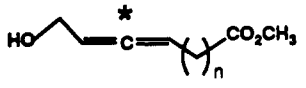
A general, high yield synthesis of multigram quantities of the title allenic alcohols is described. Intermediate **5**, derived from D-mannitol, was elaborated to both enantiomers (**10** and **11**) of the antifungal constituent (**11**) of *Sapium japonicum* and the lower homologue (**16**) useful for the synthesis of allenyl prostaglandins. The natural material was thus shown to possess the *R* configuration. The product allenes were formed in >94% ee as determined by ^{13}C NMR spectral analysis of the corresponding Mosher esters.

Introduction

During work directed toward the synthesis of medicinally important allenyl prostanoic acid derivatives,[2] we required optically active α-allenic alcohols **1** containing the ω ester functionality. It is known that various organometallic reagents react with chiral propargylic derivatives to form optically active allenes[3] (eq 1). The reaction has been successfully applied to acetates,[4] carbamates,[5] sulfinates,[6,7a] sulfonates,[6,7b] halides,[8] and ethers.[9] It is gen-



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