Photoinduced Electron Transfer Reactions of α-Cyclopropyl- and α-Epoxy Ketones. Tandem Fragmentation−Cyclization to Bi-, Tri-, and Spirocyclic Ketones

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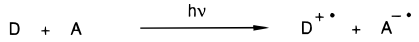
Reductive photoinduced electron transfer (PET) reactions have been performed with various bicyclic α-cyclopropyl-substituted ketones and tertiary amines. The reaction resulted in a regioselective cleavage of one cyclopropyl bond under formation of an exocyclic radical with an endocyclic enolate unit. In the case of bicyclic ketones with an unsaturated side chain, various bicyclic, spirocyclic, and tricyclic products are accessible via radical cyclization, depending on the position of the alkenyl substituent. In addition to triethylamine, *N*-silylated amines have also been used as electron donors, leading to a variety of compounds, among them are silylated fragmentation products, indicating that a proton is transferred from not only the amine radical cation but also the cationic silyl group. The intramolecular Paternó−Büchi reaction has also been studied for cyclopropane derivatives of the jasmone type leading to tetracyclic oxetanes. Finally, α-epoxy-substituted ketones have been investigated under PET conditions, yielding ring-opened products.

Introduction

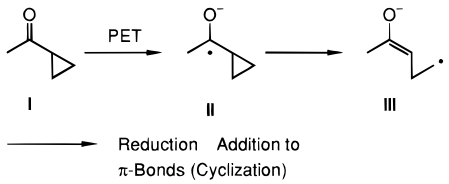
The search for synthetic, useful photoinduced electron transfer (PET) reactions is continuously increasing in organic synthesis.[1−7] The often observed high selectivity can be achieved by activating only one reactant under mild conditions. Starting from neutral compounds, the PET reaction leads to the formation of a radical ion pair (Scheme 1) of which the fate depends on the rate of back electron transfer, the solvent, the added salts, and the spin multiplicity.[8]

Earlier examples were concerned with the photoreactions of ketones with amines[9−12] and alkenes,[13] leading to the ketyl radical anion and to the corresponding donor radical cation. Alternatively, ketyl radical anions can also be formed by various methods like electrochemical reduction,[14] dissolved sodium or potassium in liquid ammonia,[15] naphthalene sodium[16,17] or samarium diiodide.[18] Due to our general interest in PET processes[3] and starting from PET reductive cleavage and cyclization reactions of cyclohexenones,[19] we have recently reported a preliminary investigation of α-cyclopropyl-substituted ketones.[3d,20] The concept of this new PET reductive cleavage reaction[19] is shown in Scheme 2. The driving force is gained from the fast cyclopropylcarbinyl−homoallyl rearrangement[21,22] ($k = 10^8$ s^{-1}) and the generation of an enolate, altogether leading to a distonic radical anion.

Scheme 1



Scheme 2



Linking **I** to an appropriate unsaturated side chain a cyclization via the radical center of **III** would be feasible

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(1) Mattes, S. L.; Farid, S. *Org. Photochem.* **1983**, *6*, 233.

(2) Mariano, P. S. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; p 145.

(3) (a) Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 825. (b) Mattay, J. *Synthesis* **1989**, 233. (c) Müller, F.; Mattay, J. *Chem. Rev.* **1993**, *93*, 99. (d) Albrecht, A.; Averdung, J.; Bischof, E. W.; Heidbreder, A.; Kirschberg, Th.; Müller, F.; Mattay, J. *J. Photochem. Photobiol., A* **1994**, *82*, 219. (e) Hintz, S.; Heidbreder, A.; Mattay, J. *Top. Curr. Chem.* **1996**, *177*, 77.

(4) *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, p 1.

(5) Karvarnos, G. J. *Fundamentals in Photoinduced Electron Transfer*; VCH Publishers: New York, 1993; p 1.

(6) Pandey, G. *Top. Curr. Chem.* **1993**, *168*, 175.

(7) Mizuno, K.; Otsuji, Y. *Top. Curr. Chem.* **1994**, *169*, 301.

(8) Mattay, J.; Vondenhof, M. *Top. Curr. Chem.* **1991**, *159*, 219.

(9) (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403. (b) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6142, 6542. (c) Simon, J. D.; Peters, K. S. *Acc. Chem. Res.* **1984**, *17*, 277.

(10) (a) Belotti, D.; Cossy, J.; Pete, J.-P.; Portella, C. *J. Org. Chem.* **1986**, *51*, 4196. (b) Cossy, J. *Pure Appl. Chem.* **1992**, *64*, 1883. (c) Cossy, J.; Furet, N.; Bouzbouz, S. *Tetrahedron* **1995**, *51*, 11751.

(11) Hasegawa, T.; Miyata, K.; Ogawa, T.; Karakizawa, A.; Komiyama, M.; Nishizawa, K.; Yoshioka, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 901.

(12) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233.

(13) (a) Gersdorf, J.; Mattay, J. *J. Photochem.* **1985**, *28*, 405. (b) Gersdorf, J.; Mattay, J.; Görner, H. *J. Am. Chem. Soc.* **1987**, *109*, 1203. (c) Mattay, J.; Gersdorf, J.; Buchkremer, K. *Chem. Ber.* **1987**, *120*, 307.

(14) (a) Shono, T.; Mitani, M. *J. Am. Chem. Soc.* **1971**, *93*, 5284. (b) Shono, T.; Nishiguchi, I.; Ohmizu, H.; Mitani, M. *J. Am. Chem. Soc.* **1978**, *100*, 545. (c) Shono, T.; Kise, N.; Fujimoto, T.; Tominaga, N.; Mitani, M. *J. Org. Chem.* **1992**, *57*, 7175.

(15) Coates, R. M.; Senter, P. D.; Baker, W. R. *J. Org. Chem.* **1982**, *47*, 3597.

(16) Pradham, S. K.; Kadam, S. R.; Kolhe, J. N. *J. Org. Chem.* **1981**, *46*, 2622, 2633.

(17) Pattenden, G.; Teague, S. J. *Tetrahedron Lett.* **1982**, *23*, 5471.

(18) (a) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29. (b) Molander, G. A.; McKie, J. A. *J. Org. Chem.* **1995**, *60*, 872.

(19) (a) Bischof, E. W.; Mattay, J. *Tetrahedron Lett.* **1990**, *31*, 7137. (b) Mattay, J.; Banning, A.; Bischof, E. W.; Heidbreder, A.; Runsink, J. *Chem. Ber.* **1992**, *125*, 2119.

(20) (a) Kirschberg, Th.; Mattay, J. *Tetrahedron Lett.* **1994**, *35*, 7217. (b) Kirschberg, Th.; Mattay, J. *Photochemical Key Steps in Organic Synthesis*; Mattay, J., Griesbeck, A. G., Eds.; Verlag Chemie: Weinheim, 1994; p 67. (c) Bischof, E. W.; Mattay, J. *J. Photochem. Photobiol., A* **1992**, *63*, 249.

(21) Bowry, U. W.; Lusztik, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687.

(22) Nonhebel, D. *Chem. Soc. Rev.* **1993**, *22*, 347.

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as a secondary step. A favored process could be the well-known 5-*exo* cyclization of 5-hexenyl radicals.[23−26] Due to the position of the unsaturated side chain, both annealated and spirocyclic ring systems should be accessible. In addition, the enolate of the radical anion **III** could be trapped by an oxophile like TMS^+ to yield silyl enol ethers. For this purpose, *N*-silylated amines as donors were also tested. The radical cations of these compounds are supposed to transfer the cationic trimethylsilyl group to the carbonyl oxygen. Furthermore we investigated α-epoxy-substituted ketones of which the PET chemistry is not yet completely understood. Analogous to the cyclopropane system, the formation of an enolate beside an oxygen-centered radical is expected.[27] Alternatively, an α-acyl radical beside a negatively charged former epoxy oxygen might be formed.[28]

Results and Discussion

Cleavage of α-Cyclopropyl Ketones by Reductive PET. Since our main interest was to perform intramolecular cyclization reactions of the intermediate **III**, it was important first to determine the regioselectivity of the cyclopropyl bond cleavage if the α-cyclopropyl system is incorporated into a bi- or polycyclic system. For this purpose, compounds **1**−**3** were synthesized. For **1** and **2** we used Corey's cyclopropanization method[29] starting from the corresponding enones. Compound **3** was synthesized according to the methods reported in the literature from cyclohexadiene and acrylonitrile.[30] The PET reaction was performed by irradiation at 300 nm with Pyrex-filtered light to get a clean nπ^* excitation of the carbonyl compound using an excess of triethylamine as the electron donor.[31,32]

All three compounds undergo regioselective ring opening of the so-called *exo*-cyclic C−C bond. The monocyclic products **4** and **5** are formed via primary radicals of the type **V** rather than the more stable tertiary radical[33] of an alternative *endo*-cyclic ring opening (Scheme 3). The results are summarized in Table 1. Obviously, stereoelectronic effects control this course of reaction because of a favorable interaction between the SOMO (2p orbital at C of the ketyl radical anion) and the antibonding orbitals of the *exo*-cyclic cyclopropane bond.[3d] Unlike the MO's of the *endo*-cyclic cyclopropane, the C−C bond and the 2p orbital in the *exo*-cyclic compound are orthogonal. In addition, cleavage of this latter bond would lead to ring-enlarged systems increasing the strain energy.[34] For only two derivatives of bicyclo[4.1.0]heptan-5-ones substituted by a methoxycarbonyl group in position 1 has this type of thermodynamically-driven reaction been observed.[19,35] In both cases the strained ring (cyclobutane or cyclopropane) is substituted at C-3 by a methoxycarbonyl group.

Analogously, the PET reductive cleavage of **3** leads to the bicyclo[3.3.0]octan-3-one **6**. However, we did not observe the high yield of 79% reported by Pandey and co-workers.[36]

Tandem Fragmentation−Cyclization of α-Cyclopropyl Ketones with an Unsaturated Side Chain. Our concept of the tandem fragmentation−cyclization is illustrated in Scheme 4 for unsaturated bicyclo[2 + *n*.1.0]-alkanones ($n = 1, 2$). Irradiation of **VI** in the presence of triethylamine in acetonitrile ($\lambda > 300$ nm) leads to the ketyl radical anion **VII** which is subjected to a regioselective cleavage of the cyclopropane. The distonic radical anion **VIII** cyclizes to **IX** in a radical process. Finally, the product **X** is formed after protonation and H-abstraction.[37] Depending on the position of the unsaturated side chain, various annealated and spirocyclic ketones are accessible by this method. In the following, we first describe the synthesis of the starting materials.

Synthesis of 4-Allyl Cyclopropyl Ketones 13 and 14. 3-Ethoxycyclopent-2-enone (**7**)[38] and 3-ethoxycyclo-

Scheme 3

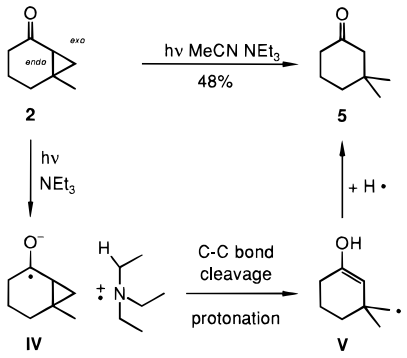
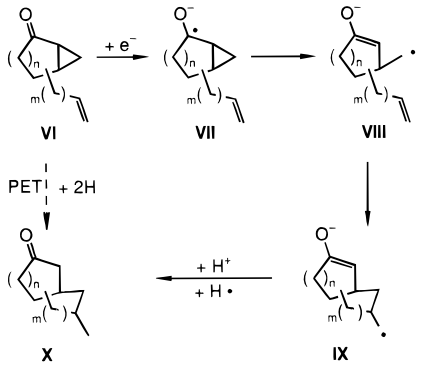


Table 1. Ring Opening of Cyclopropyl Ketones by Reductive PET Reactions

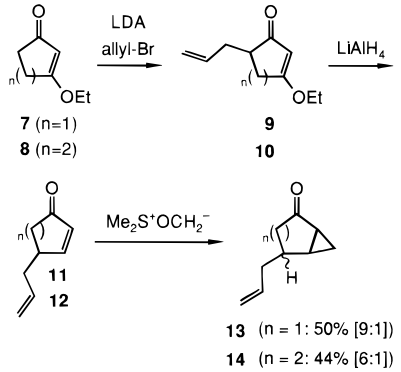
entry	starting material	product	yield
1	**1**	**4**	39 %
2	**2**	**5**	48 %
3	**3**	**6**	36 %

(23) Baldwin, J. E.; Cutting, J.; Dupont, W.; Kruse, L.; Silberman, L.; Thomas, R. C. *J. Chem. Soc., Chem. Commun.* **1976**, 734, 736.
(24) (a) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (b) Beckwith, A. L. J. *Chem. Soc. Rev.* **1993**, *22*, 143.
(25) (a) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553. (b) Giese, B. *Radicals in Organic Synthesis. Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986; p 141.
(26) Curran, D. P. *Synthesis* **1988**, 417, 489.
(27) Cossy, J.; Bouzide, A.; Ibhi, S.; Aclinon, P. *Tetrahedron* **1991**, *47*, 7775.
(28) Hasegawa, E.; Ishiama, K.; Horaguchi, T.; Shimizu, T. *J. Org. Chem.* **1991**, *56*, 1631.
(29) Corey, E. J.; Chaycovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.
(30) (a) Demuth, M.; Mikhail, G. *Synthesis* **1985**, 145. (b) Demuth, M. *Photochemical Key Steps in Organic Synthesis;* Mattay, J., Griesbeck, A. G., Eds.; Verlag Chemie: Weinheim, 1994; p 73.
(31) At shorter wavelengths (<300 nm) photoionization of the triethylamine cannot be excluded similar to PET processes in hexamethylphosphoric acid triamide (HMPA)—cf. ref 32 and H. H. Morrison, Purdue University, private communication.
(32) (a) Dornhagen, J.; Klausener, A.; Runsink, J.; Scharf, H.-D. *Liebigs Ann. Chem.* **1985**, 1838. (b) Klausener, A; Beyer, G.; Leismann, H.; Scharf, H.-D.; Müller, E.; Runsink, J.; Görner, H. *Tetrahedron* **1989**, *45*, 4989.
(33) Viehe, H. G.; Janousek, Z.; Merenyi, R. *Substituent Effects in Radical Chemistry*; D. Reidel Publishing Co: Dordrecht, 1986; p 1.
(34) Haufe, G.; Mann, G. *Chemistry of Alicyclic Compounds*; Elsevier: Amsterdam, 1989; p 87.
(35) Cossy, J.; Furet, N. *Tetrahedron Lett.* **1993**, *34*, 8107.
(36) Pandey, B.; Rao, A. T.; Dalvi, P. V.; Kumar, P. *Tetrahedron* **1994**, *50*, 3843.
(37) In Scheme 4 one plausible mechanism is suggested. Alternatively, protonation may take place before C−C bond cleavage or cyclization.

Scheme 4



Scheme 5



hex-2-enone (**8**)[39] were alkylated with allyl bromide under kinetic deprotonation conditions. Reduction of **9** and **10** by lithium aluminum hydride[40] followed by the Corey−Chaycovsky procedure[29] gave **13** and **14** in good yield (Scheme 5). On the basis of the NMR analysis (in 1:1 benzene-d_6/$CDCl_3$, H−H COSY, ^1J(CH)-correlated, NOE), the *trans*-isomers were shown to be the major diastereoisomer. An enhancement of the intensity of the C5−H was observed after saturating the *endo*-cyclic C7−H and vice versa (Figure 1).

Synthesis of 2-Allyl Cyclopropyl Ketones 25 and 26. In general, two procedures have been developed for the synthesis of 2-alkylated cycloalkenones. The first starts with a Birch reduction of an appropiate anisole derivative.[41,42] We have applied the second strategy using the Stille reaction of a 2-iodocycloalkenone and allyl bromide as the key step (Scheme 6). The α-bromocycloalkenone ketals **19** and **20** were synthesized from 2-cyclopentenone **15** and 2-cylohexenone **16**. The following procedures are already reported in the literature[43,44] and were slightly modified to obtain the 2-allylcycloalkenones **23** and **24.** Applying the sulfur ylide method, the starting materials **25** and **26** are accessible in overall good yield. Compound **28** was obtained from the commercially available *cis*-jasmone (**27**).

Synthesis of 3-Alkenylbicyclo[4.1.0]heptan-5-ones 31 and 32. Grignard reaction of 3-ethoxycyclohexenone (**8**) with ω-bromoalkenes[45] gave the 3-alkenyl-substituted

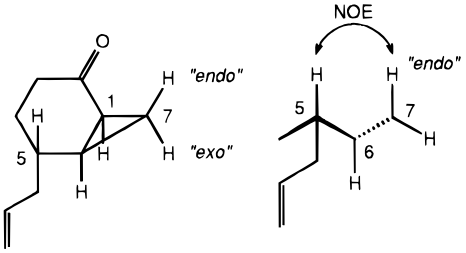
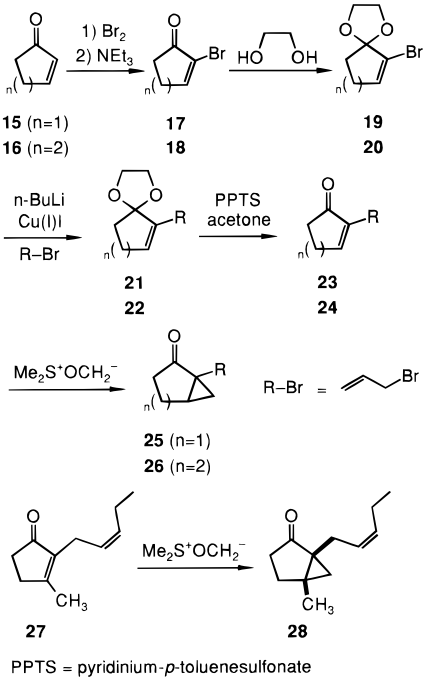
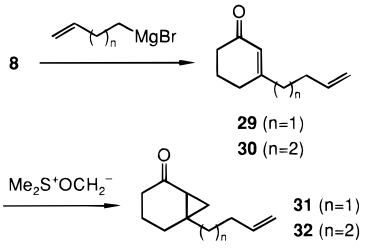


Figure 1.

Scheme 6



Scheme 7

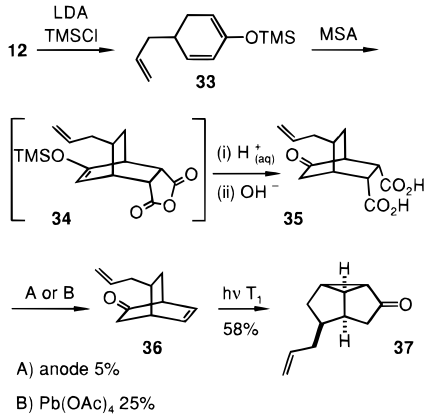


enones **29** and **30**[46] which were converted to **31** and **32** as usual (Scheme 7).

Synthesis of 6-Allyltricyclo[3.3.0.0^{2,8}]octan-3-one (37). The oxadi-π-methane rearrangement[30] is used as the key step in the synthesis of **37**. Quenching the kinetically deprotonated compound **12** with trimethylsilyl chloride yielded the trimethylsilyl enol ether **33** which was subjected to a Diels−Alder reaction with maleic anhydride. The attack was expected to occur from the nonhindered side in the typical *endo* mode. The hydrolysis of the silyl enol ether and the anhydride was performed in one step. The yield-determining step of the total synthesis was the bisdecarboxylation of **35**. Although the electrochemical method had been successfully applied in similar cases,[47] we obtained **36** in only a poor yield of

(38) Fuchs, R.; McGarrit, J. *Synthesis* **1992**, 373.
(39) Gannon, W. F.; House, H. O. *Org. Synth.* **1960**, *40*, 41.
(40) Stork, G.; Danheiser, R. L. *J. Org. Chem.* **1973**, *38*, 1775.
(41) Wilds, G.; Nelson, B. *J. Am. Chem. Soc.* **1953**, *75*, 5360.
(42) Taber, D. F.; Gunn, P. B.; Chin, I. C. *Org. Synth.* **1983**, *61*, 59.
(43) Smith, A.; Branca, S.; Guaciaro, M.; Wovkilich, P.; Korn, A. *Org. Synth.* **1983**, *61*, 65.
(44) Ladlow, M.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1107.
(45) Kraus, G. A.; Landgrebe, K. *Synthesis* **1984**, 885.
(46) Becker, D.; Harel, Z.; Nagler, M.; Gillon, A. *J. Org. Chem.* **1982**, *47*, 3297.
(47) Warren, C. B.; Bloomfield, J. J.; Chikos, J. S.; House, R. A. *J. Org. Chem.* **1973**, *38*, 4011.

Scheme 8



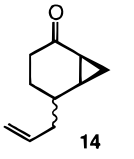
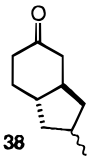
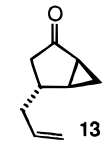
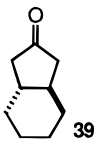
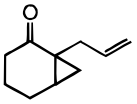
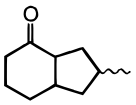
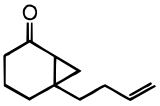
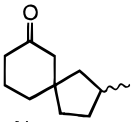
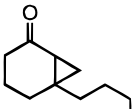
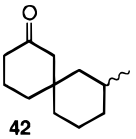
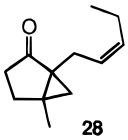
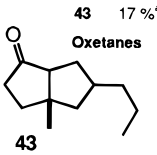
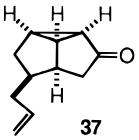
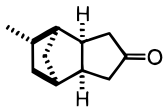
5%. On the other hand, the procedure using lead tetraacetate[48] gave better results with an isolated yield of 25%. The triplet-sensitized rearrangement of **36** yielded **37** without formation of any side products (Scheme 8).

Tandem Fragmentation−Cyclization Reactions by Reductive PET. The results of the tandem fragmentation−cyclization reaction of various α-cyclopropyl ketones bearing an unsaturated side chain are summarized in Table 2. Bicycloalkanones derived from cyclohexenone and cyclopentenone undergo this type of reductive rearrangement independent of the position of the side chain (α, *β*, and *γ*). However, the mode and the efficiency of the cyclization process depend on structural features of the starting material. For example, **14** cyclizes to **38** following the well-established 5-*exo*-trig mode. Similar behavior is seen with **28**, **31**, and **37**, leading to either annealated or spirocyclic and briged ring systems. On the other hand, compound **13**, which resembles **14**, rearranges to **39** in a 6-*endo* fashion. Obviously, the stereochemical arrangement of the allyl group and the cyclopropane (*trans*) controls the mode of cyclization, leading to a *trans*-fused bicyclo[4.3.0]nonanone. In the case of a 5-*exo* cyclization, an unfavorable *trans*-bicyclo[3.3.0]octanone would have been formed. In general, a cyclization to a cyclohexanone proceeds with low efficiency (e.g., **13** → **39** and **32** → **42**), leading to large amounts of polymeric material. We also tested the scope of the SmI_2 method. However, in most cases, the procedure gives lower yields compared to the PET method. In the case of **37**, even the SmI_2 method failed to give the rearranged product **44**. Only if the photochemical competition decreased the efficiency of the fragmentation−cyclization process would this stochiometric reduction gives better results. Whereas the *cis*-jasmone derivative (**28**) leads to a mixture of rearrangement **43** and oxetane products, under PET conditions only **43** is formed with SmI_2. For reasons of clarity, the proposed mechanism for the formation of **44** is shown in Scheme 9.

Generally, the stereochemistry of the substituents is preserved during the rearrangement, and in addition, in most cases, one diastereomer is preferentially formed during the cyclization step (e.g., **38** in a 9:1 ratio). In case of the *exo* cyclizations, the relative stereochemistry of the methyl group could not be assigned. Only a comprehensive NMR analysis of **44** allowed its stereochemical assignment. In Figure 2 the decisive NOE experiments of **44** are shown.

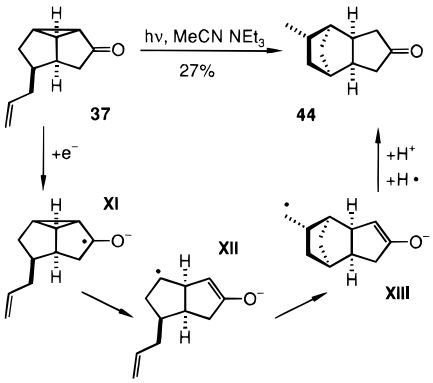
(48) Wolinski, J.; Login, R. B. *J. Org. Chem.* **1972**, *37*, 121.

Table 2. PET Reaction (Tandem Fragmentation−Cyclization)

entry	starting material	product	yield
1			23 %[a] (9:1) 13 %[c]
	14	38	
2			20 %[b]
	13	39	
3			35 %[a] (2:1)
	26	40	
4			41 %[b] (2:1)
	31	41	
5			8 %[b] (3:1)
	32	42	
6			43 17 %[a], 44 %[c] Oxetanes 34 %[a,d]
	28	43	
7			27 %[b]
	37	44	

[a] Isolated yield referring to starting material consumed. [b] Isolated yield. [c] Reaction with SmI_2. [d] For structure of oxetanes see Table 3 (**45**, **46**).

Scheme 9



Intramolecular Oxetane Formation. The oxetanes that were formed from **28** as well as **43** were of great interest to us because of their complex structure. We decided to test the reaction in the absence of any electron donor in order to avoid the formation of the fragmentation−cyclization product **43** (Table 3). The irradiations

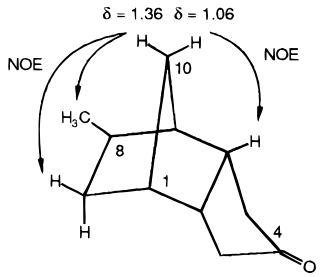
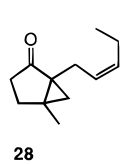
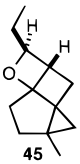
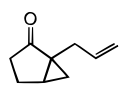


Figure 2.

Table 3. Intramolecular Paterno–Büchi Reaction

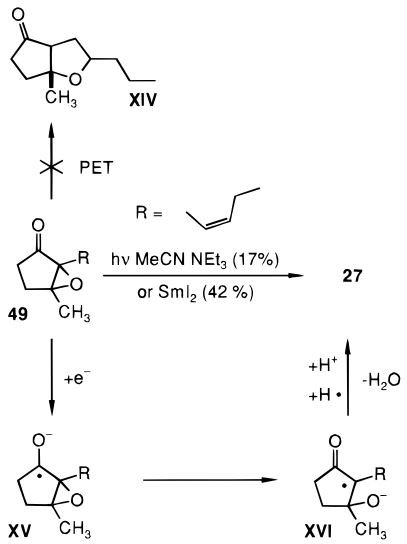
entry	starting material	products	yield
1		 	**45** 36 % **46** 6 %
	28	**45** **46**	
2		 	**47** 50 % **48** 5 %
	25	**47** **48**	

were performed in benzene solution using Pyrex-filtered light of a wavelength >300 nm. Two diastereomeric oxetanes **45** and **46** (3.2:1) were formed in nearly quantitative yield (confirmed by a NMR spectra of the crude mixture). The smaller isolated yield was caused by decomposition of the products during the workup procedure. The assignment of **45** and **46** as *straight* adducts (head-to-head) was confirmed on the basis of the NMR experiments. The vicinal relationship of the 3-H and 4-H protons as well as the methylene protons of the ethyl substituent was confirmed using homonuclear decoupling techniques. In the case of **45**, the vicinal coupling of 2.1 Hz between 3-H and 4-H is consistent with a dihedral angle of 90° between these protons. For **46**, however, the coupling constant of 6.7 Hz between 3-H and 4-H indicates a dihedral angle of roughly 0°.

We also synthesized the unsubstituted 2-oxatetracyclo-[4.4.0.$0^{1,4}$.$0^{6,8}$]decane. Irradiation of **25** in benzene in the absence of any electron donor led to the formation of the two isomeric compounds **47** and **48** (8:1) in nearly quantitative yield (Table 3). Again, the decreased isolated yield was due to the instability of the material upon workup. Compound **47** was assigned as *straight* oxetane because of its similarity to **45** and **46**. In addition, the vicinal coupling constants of 6.2 and 2.1 Hz of 4-H support this structure. The minor adduct **48** was isolated only in a very small amount because it is even less stable than **47**. The assignment as a *crossed* oxetane was mainly based on the chemical shifts in the ^{13}C NMR spectra (e.g., low-field shifted signal of tertiary carbon at δ = 88.5 ppm). Additional low-field ^{1}H resonances at 5.31, 4.97, and 4.77 ppm indicate a close proximity to oxygen and, therefore, support the *crossed* structure.

Our findings resemble a report of Kossanyi et al. concerning photoreactions of 2-allylcyclopentanone.[49] The authors observed the formation of both *crossed* and *straight* oxetanes in nearly equal amounts. Obviously, the geometric flexibility is restricted by the cyclopropane ring leading to the preferred formation of the *straight* adducts in our case.

Scheme 10



PET Reactions of α-Epoxy Ketones. In addition to the α-cyclopropyl ketones, the corresponding α-epoxy ketones were of interest to us. These compounds provide access to tetrahydrofuran systems assuming an analogous fragmentation–cyclization process would operate (**49** → XIV). As an easily accessible model for this assumption, we chose the α-epoxy derivative **49** of *cis*-jasmone **27**.

The PET reaction of **49** in the presence of TEA yielded jasmone after chromatography on silica. We assume a mechanism involving a radical anion **XVI** as the key intermediate (Scheme 10). The lack of cyclization in the course of the reaction is ascribed to the high negative charge density on the foremost epoxy group rather than the enolate. Earlier reports of Hasegawa[28] and Cossy[29] support our hypothesis. Furthermore, the alternative reduction using SmI_2 yielded the same product even upon substitution of the DMPU by HMPA or running the reaction at a lower temperature of −78 °C. The electron transfer mechanism is also supported by the already observed photoreaction of α-epoxy ketones with allyltributyltin leading to products which result from a C–O rather than a C–C bond cleavage.[50]

***N*-Silylamines as Electron Donors.** So far triethylamine was used as the reducing agent providing not only the electron but most probably the proton and eventually even the hydrogen during the fragmentation–cyclization sequence (cf. Scheme 3 and 4). Another leaving group which may act as electrofuge is the trimethylsilyl group. Whereas α-silylated amines have been used already by Mariano and co-workers,[12,51,52] the behavior of *N*-silylated amines is unknown so far. Therefore, we used these compounds as electron donors, hoping that the silyl group might be transferred to the oxygen of the former ketone.

The first results obtained in the reaction of **2** with a 5-fold excess of *N*,*N*-dimethyl(trimethylsilyl)amine (**Me_2NTMS**) were quite encouraging. The silyl enol ether

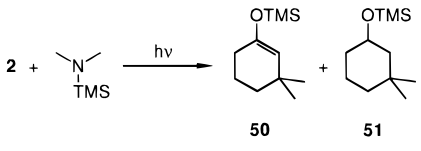
(49) (a) Kossanyi, J.; Jost, P.; Furth, B.; Daccord, G.; Chaquin, P. *J. Chem. Res., Synop.* **1980**, 368. (b) Furth, B.; Daccord, G.; Kossanyi, J. *Tetrahedron Lett.* **1975**, *48*, 4259.

(50) Hasegawa, E.; Ishiyama, K.; Horaguchi, T.; Shimizu, T. *Tetrahedron Lett.* **1991**, *32*, 2029.

(51) Xu, W.; Zhang, X.-M.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 8863.

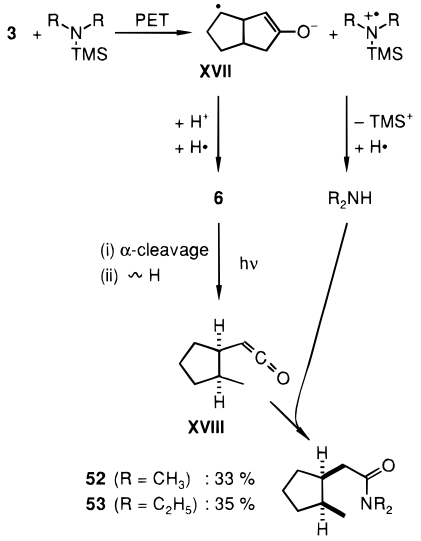
(52) Pandey, G.; Reddy, G. D.; Kumaraswamy, G. *Tetrahedron* **1994**, *50*, 8185.

Scheme 11



Ratio **2** : Me_2NTMS	Yield (Main Product)	Ratio **50** : **51**
1 : 5	34 %	5 : 1
1 : 1	22 %	1 : 5

Scheme 12

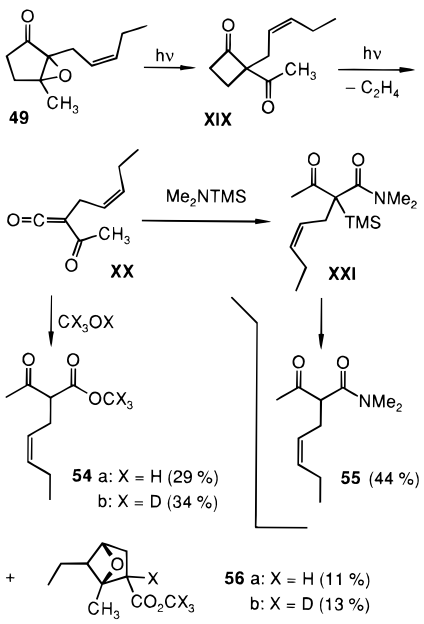


50 was formed in 34% yield along with **51** in smaller amounts (Scheme 11). On the other hand, **51** became the major product after PET reaction in the presence of only 1 equiv of **Me_2NTMS**. The thermal formation of either product could be excluded on the basis of control experiments.

We assume a similar mechanism as that shown in Scheme 3 for the corresponding reaction with triethylamine. The key steps are PET and the transfer of the TMS cation to the ketyl radical anion or the enolate, respectively. This reaction may proceed "S_N2-like" due to the high concentration of the silylated amine. The mechanism of the formation of the ether **51** is still unclear. Since it is preferentially observed at lower concentrations of the amine which favors dissociation of the primarily generated radical ion pair, it might be formed from the ring-opened cyclohexanone **5** in a secondary process after reduction to the alcohol. The photoreduction of ketones to secondary alcohols in acetonitrile containing triethylamine had already been described by us in an earlier paper.[19c] Later, Cossy and Furet confirmed this observation.[35] Similarily, **5** could be reduced to either its alcohol followed by silylation in the presence of Me_2NTMS or its radical cation.

The PET reactions of **3** with one equivalent of silylated amines took unexpected courses. The only products which could be isolated in up to 35% yield were the ring-opened amides **52** and **53**. The *cis* relationship of the two substituents was verified on the basis of the coupling constant of 7.1 Hz between 1-H and 2-H which is typical for dihedral angles of roughly 0°. In Scheme 12, a plausible mechanism is shown which is further supported by the following control experiments: Irradiation of **6** in acetonitrile and in the presence of diethylamine produced **53** as the only product. However, there is no direct path from **3** to the ring-opened products since photolysis of **3** in acetonitrile containing 24 equiv of methanol yielded several products, of which not one was identified as the methyl ester analogue of the amides **52** and **53**.

Scheme 13



Similarily, we investigated the reaction of epoxyjasmone (**49**) with **Me_2NTMS** (5-fold excess). After chromatographic purification, **55** was isolated in 44% yield. The same experiment, however, in the presence of methanol or methanol-d_4 provided the esters **54** and the oxetane **56**. These results support the formation of a ketene intermediate (**XX** in Scheme 13). Therefore, we assume the following mechanism: In a first photochemical event, the epoxy ketone **49** rearranges by ring contraction via **XIX** and loss of ethylene to the ketene **XX**, similar to the findings of Marcos, Reusch, and Gibson.[53,54] The reaction of ketenes with *N*-silylated amines is known. For example, ketene itself yields *N*,*N*-dimethyl-2-(trimethylsilyl)acetamide upon reaction with **Me_2NTMS**[55] and even diketene shows similar reactions.[56] Therefore, we assume an addition of **Me_2NTMS** to **XX** under formation of **XXI** which decomposes under our workup procedures to **55**. The scavenging experiments with CH_3OH and CD_3OD support our proposed mechanism. In summary, with α-epoxy ketones of the type **49** and *N*-silylated amines, the photoinduced rearrangement efficiently competes with a PET process.

Conclusion

α-Cyclopropyl ketones cleave homolytically one C−C bond of the three-membered ring during the course of the PET reaction with triethylamine. In the presence of a well-chosen unsaturated side chain, a cyclization is feasable to yield ring-annealated or spirocyclic products. This reaction represents an example of the extensively studied tandem (domino, cascade) reactions.[57] The reaction of the α-epoxy ketone **49** with triethylamine is assumed to proceed via an α-acyl radical as the most

(53) Marcos, C. S.; Reusch, W. *J. Am. Chem. Soc.* **1967**, *89*, 3363.
(54) Gibson, T. *J. Org. Chem.* **1974**, *39*, 845.
(55) Sheludyakov, V. D.; Kozyukov, V. P.; Pretrovskaya, L. I.; Mironov, V. F. *Khim. Geterotsikl. Soedin.* **1967**, *1*, 185; *Chem. Abstr.* **1967**, *67*, 43858.
(56) Bankov, Y. I.; Burlachenko, G. S.; Kostyuk, A. S.; Lutsenki, I. F. *Zh. Obshch. Khim.* **1966**, *36*, 1859; *Chem. Abstr.* **1967**, *66*, 65576z.

reasonable intermediate. The preliminary results obtained in the photochemical reaction of α-cyclopropyl ketones as well as α-epoxy ketones with the *N*-silylated amines showed a complex behavior depending mainly on the nature of the carbonyl compound. The expected formation of silyl enol ethers is not an exclusive reaction pathway. In addition, an acetamide function was accessible during the photochemical excitation of a carbonyl group in the presence of the *N*-silylated amines via either a direct addition of the amine to a ketene or the addition of the dialkylamine derived in the course of the reaction from a loss of the silyl group. Furthermore, the intramolecular oxetane formation from **25** and **28** has been studied, which showed a remarkable regioselectivity. This behavior was explained by the presence of the cyclopropyl moiety imposing some steric demands on the starting material.

Experimental Section

Standard Procedures. All solvents were dried according to standard procedures. Benzene (pro analysis), chloroform (pro analysis), and pyridine (dry) were used as purchased. Samarium diiodide solution was puchased from Fluka. The irradiations were performed in a Rayonet photoreactor (Southern New England) fitted with 300 nm lamps using Pyrex or quarz tubes of ca. 12 mL volume. Abbreviations used are the following: pe, petrol ether; e, ether; ch, cyclohexane; ee, ethyl acetate.

General Procedure A (Cyclopropanization of Enones). A portion (1.1 molar equiv) of sodium hydride dispersion in mineral oil (55−65%) was washed three times with petroleum ether. Traces of the solvent were removed under reduced pressure. An argon atmosphere was introduced, and 1.1 molar equiv of trimethylsulfoxonium iodide was added followed by dry DMSO (2 mL/1 mmol of enone). The solution was stirred for 30 min, until the evolution of hydrogen ceased. The enone was added, dissolved in dry DMSO (1 mL/10 mmol of enone), and the solution was stirred at room temperature for 4 h. The mixture was poured onto ice water and extracted with ether (four times). The combined organic layers were washed with water and brine and dried over magnesium sulfate. The products were isolated using column chromatography on silica.

General Procedure B (Epoxydation of Enones). A solution of 7.0 mmol of the enone in 10 mL of methanol was cooled to 0 °C, and 4.8 mL of 30% hydrogen peroxide was added. This solution was treated with a mixture of 0.8 mL of 6 M NaOH and 8.0 mL of methanol. After the mixture was stirred for 3 h at room temperature, the solution was poured onto ice water and extracted three times with ethyl acetate. The combined organic layers were washed with saturated $NaHCO_3$ solution and brine and were dried over Na_2SO_4. The epoxide was isolated after column chromatography using silica.

General Procedure C (PET Reaction with Triethylamine). The solutions of the cyclopropyl ketones, triethylamine (4−5 equiv), and decane (internal standard) in dry acetonitrile were placed in several tubes, degassed, and irradiated. The reaction course was monitored by TLC and GLC. In a typical reaction, the best results were obtained after roughly 5 days of irradiation time. After removal of the solvent under reduced pressure, the products were isolated by HPLC or column chromatography.

General Procedure D (Photochemical Transformation in the Presence of *N*-Silylated Amines). Dried and cooled quartz reaction tubes (15 mL of volume) were filled with 1 mmol of the ketone, 1 mmol or 5 mmol of the *N*-silylated amines, and 12 mL of dry acetonitrile. During irradiation, the reaction was monitored by GLC. After complete disappearance of the starting material, the solvent was removed under reduced pressure and the products were isolated by column chromatography using either silica or Al_2O_3 (neutral).

General Procedure E (SmI_2 Reduction According to Motherwell). A 1 mM solution of SmI_2 in THF was added to a THF solution (13 mL) of 1.0 mmol of the ketone and 3 mL of DMPU under argon atmosphere until the color turned violet. The reaction was quenched by addition of a saturated, aqueous solution of $NaHCO_3$. Extraction with ether, washing with water and brine, and drying over $MgSO_4$ gives the product solution.

General Procedure F (SmI_2 Reduction). The same reaction conditions as in procedure E were applied. The only variation was introduced upon work up. The blue solution which was obtained after the addition of the SmI_2 solution was quenched by adding only 1 mL of saturated $NaHCO_3$ solution which caused the separation of a clear solution and solid samarium hydroxide. The THF was removed under reduced pressure, and 50 mL of ether and 20 mL of water were added. The aqueous solution was further extracted with ether, and the combined organic layers were washed with brine and dried over magnesium sulfate. The products were isolated using either HPLC or column chromatography on silica.

Synthesis of the Starting Materials: 1-Methylbicyclo[3.1.0]hexan-4-one (1). The cyclopropanization reaction (procedure A) of 4.22 g (43.0 mmol) of 3-methylcyclopentenone yielded 1.85 g (39%) of **1** after chromatography on Al_2O_3 (eluent: pe/e 8:2): IR (neat) 2920 (s) cm^{-1}, 2860, 1715 (s, C=O), 1285, 1175, 1020, 895, 770; ^1H NMR (300 MHz, $CDCl_3$) δ 1.12 (m, 2 H), 1.35 (s, 3 H, CH_3), 1.60 (dd, J = 4.5, 5.0 Hz, 1 H), 1.86−2.20 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1 (CH_2), 21.4 (CH_3), 29.2 (CH_2), 30.2 (Cq), 32.8 (CH_2), 35.2 (CH), 215.0 (Cq); MS (70 eV) m/z = 111 (M^+ + 1, 12), 110 (M^+, 30), 82 (58), 67 (100), 39 (81); UV (acetonitrile) λ_{max}= 208 nm (ϵ_{max} = 4080), λ = 268 nm (ϵ = 185). Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.87; H, 9.29.

1-Methylbicyclo[4.1.0]heptan-5-one (2). The cyclopropanization reaction (procedure A) of 5.5 g (50.0 mmol) of 3-methylcyclohexenone yielded 2.91 g (47%) of **2** after chromatography on silica (eluent: ch/ee 95:5): IR (neat) 2940 (s) cm^{-1}, 2870, 1685 (s, C=O), 1445, 1390, 1320, 1305, 1245, 1090, 945, 865; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (dd, J = 10.3, 5.1 Hz, 1 H, 7a-H), 1.22 (s, 3 H, CH_3), 1.40 (dd, J = 4.5, 4.5 Hz, 1 H, 7b-H), 1.55−1.80 (m, 4 H), 1.90−2.10 (m, 2 H), 2.28 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.7 (CH_2, C-7), 18.3 (CH_2), 24.2 (Cq, C-1), 25.0 (CH_3), 28.3 (CH_2), 34.6 (CH, C-6), 36.1 (CH_2, C-4), 209.2 (Cq, C-5); MS (70 eV) m/z 124 (M^+, 38), 81 (80), 68 (100), 67 (100), 55 (58), 39 (50); UV (acetonitrile) λ_{max}= 205 nm (ϵ_{max} = 5310), λ = 282 nm (ϵ = 37). Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.01; H, 9.75.

4-(Prop-2′-enyl)bicyclo[4.1.0]heptane (14). The cyclopropanization reaction (procedure A) of 1.78 g (13.0 mmol) of 4-(prop-2′-enyl)cyclohexenone (**12**) yielded 860 mg (44%) of **14** after chromatography on silica (eluent: ch/ee 93:7). The product was obtained as a 6:1 mixture (GLC) of two diastereoisomers. The spectroscopic data refer to the main isomer: IR (neat) 3060 cm^{-1}, 2900, 1680 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (ddd, J = 9.7, 8.2, 5.3 Hz, 1 H, 7-H *exo*), 1.25 (ddd, J = 5.9, 5.3, 4.6 Hz, 1 H, 7-H *endo*), 1.58−1.82 (m, 4 H, 6-H, 4-H, 1-H), 2.08−2.36 (m, 5 H, 1′-H, 5-H, 3-H), 5.03−5.12 (m, 2 H, 3′-H), 5.81 (m, 1 H, 2′-H); ^1H NMR (360 MHz, $CDCl_3$/C_6D_6 1:1) δ 0.75 (ddd, J = 9.7, 8.2, 5.3 Hz, 1 H, 7-H *exo*), 0.81 (ddd, J = 5.9, 5.3, 4.6 Hz, 1 H, 7-H *endo*), 1.17 (m, 2 H, 4a-H, 6-H), 1.41 (m, 1 H, 4b-H), 1.50 (ddd, J = 9.7, 7.6, 4.7 Hz, 1 H, 1-H), 1.70 (m, 1 H, 5-H), 1.80−2.00 (m, 4 H, 3-H, 1′-H), 4.86−4.94 (m, 2 H, 3-H), 5.60 (m, 1 H, 2′-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.5 (CH_2, C-7), 23.4 (CH_2), 23.8 (CH), 25.4 (CH), 31.3 (CH), 32.8 (CH_2), 38.9 (CH_2), 116.6 (CH_2, C′-3), 136.4 (CH, C′-2), 209.5 (Cq); ^{13}C NMR (90 MHz, $CDCl_3$/C_6D_6 1:1) δ 13.3 (CH_2, C-7), 24.6 (CH), 24.7 (CH_2, C-4), 26.4 (CH), 32.6 (CH, C-5), 33.9 (CH_2), 40.0 (CH_2), 117.5 (CH_2, C-3′), 137.5 (CH, C-2′), 209.3 (Cq); MS (70 eV) m/z 151 (M^+ + 1, 14), 150 (M^+, 10), 109 (35), 93 (30), 91 (38), 79 (82), 77 (32), 67 (62), 55 (26), 41

(57) The January issue of *Chem. Rev.* (Wender, P. A., Guest Editor) contains several examples of tandem, domino, and cascade reactions (general theme: Frontiers in Organic Synthesis): (a) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115. (b) Denmark, S. E.; Thorarensen, A. *Chem. Rev.* **1996**, *96*, 137. (c) Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167. (d) Ryu, I.; Sonoda, N.; Curran, D. P. *Chem. Rev.* **1996**, *96*, 177. (e) Parsons, P. J.; Penkott, C. S.; Skell, A. J. *Chem. Rev.* **1996**, *96*, 195. (f) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207.

(49), 39 (100). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.84; H, 9.92.

4-(Prop-2′-enyl)bicyclo[3.1.0]hexan-2-one (13). The cyclopropanization reaction (procedure A) of 250 mg (2.04 mmol) of 4-(prop-2′-enyl)cyclopentenone (**11**) yielded 140 mg (50%) of **13** after chromatography on silica (eluent: pe/e 8:2). The observed selectivity was 9:1 favoring the *trans*-isomer: IR (neat) 3070 cm^{-1}, 2900, 1720 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (ddd, J = 4.7, 4.5, 3.1 Hz, 1 H, 6-H), 1.20 (dddd, J = 8.9, 7.4, 4.8, 1.4 Hz, 1 H, 6-H), 1.72−1.83 (m, 2 H), 1.97 (ddd, J = 7.9, 4.8, 4.8 Hz, 1 H, 1-H), 2.06−2.30 (m, 3 H), 2.37 (m, 1 H), 5.03−5.13 (m, 2 H, 3′-H), 5.78 (ddt, J = 17.4, 9.5, 6.9 Hz, 1 H, 2′-H); ^1H NMR (360 MHz, C_6D_6) δ 0.39 (ddd, J = 4.6, 4.6, 3.2 Hz, 1 H, 6-H), 0.55 (dddd, J = 8.9, 7.5, 4.8, 1.3 Hz, 1 H, 6-H), 1.35 (ddd, J = 7.7, 4.7, 4.7 Hz, 1 H, 1-H), 1.46 (dddd, J = 8.7, 4.6, 3.1, 1.1 Hz, 1 H, 5-H), 1.53 (m, 1 H, 3a-H), 1.70−1.90 (m, 4 H, 3b-H, 4-H, 1′-H), 4.82−4.95 (m, 2 H, 3′-H), 5.50 (m, 1 H, 2′-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8 (CH_2, C-6), 27.0 (CH, 2×), 34.9 (CH), 37.8 (CH_2), 40.6 (CH_2), 117.3 (CH_2, C-3′), 135.4 (CH, C-2′), 214.1 (Cq, C-2); ^{13}C NMR (90 MHz, C_6D_6) δ 13.2 (CH_2, C-6), 26.6 (CH, C-1), 27.1 (CH, C-5), 35.2 (CH, C-4), 38.1 (CH_2, C-3), 41.0 (CH_2, C-7), 117.3 (CH_2, C-3′), 136.2 (CH, C-2′), 211.4 (Cq, C-2); MS (70 eV) m/z 137 (M^+ + 1, 8), 136 (M^+, 5), 108 (10), 95 (34), 79 (24), 67 (100), 65 (22), 55 (23), 41 (48), 39 (98).

1-(Prop-2′-enyl)bicyclo[4.1.0]heptan-2-one (26). The cyclopropanization reaction (procedure A) of 500 mg (4.0 mmol) of 2-(prop-2′-enyl)cyclohexenone (**24**) yielded 310 g (52%) of **26** after chromatography on silica (eluent: ch/ee 9:1): IR (neat) 3080 cm^{-1}, 2920, 2850, 1670 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (dd, J = 8.5, 5.5 Hz, 1 H, 7-H *exo*), 1.29 (dd, J = 5.5, 5.5 Hz, 1 H, 7-H *endo*), 1.54−1.73 (m, 3 H), 1.87−2.11 (m, 4 H), 2.30 (ddd, J = 17.0, 5.0, 5.0 Hz, 1 H), 2.70 (ddt, 15.0, 7.0, 1.2 Hz, 1 H), 4.92−5.03 (m, 2 H, 3′-H), 5.78 (m, 1 H, 2′-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.6 (CH_2, C-7), 19.4 (CH_2), 22.3 (CH_2), 24.2 (CH), 33.8 (Cq), 37.4 (CH_2), 37.8 (CH_2), 116.4 (CH_2, C-3′), 135.9 (CH, C-2′), 209.4 (Cq); MS (70 eV) m/z 151 (M^+ + 1, 6), 150 (M^+, 14), 91 (41), 79 (100), 77 (38), 43 (32), 39 (92). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.88; H, 9.75.

1-(Prop-2′-enyl)bicyclo[3.1.0]hexan-2-one (25). The cyclopropanization reaction (procedure A) of 440 mg (3.6 mmol) of 2-(prop-2′-enyl)cyclopentenone (**23**) yielded 360 mg (73%) of **25** after chromatography on silica (eluent: pe/e 8:2): IR (neat) 3060 cm^{-1}, 2930, 2870, 1715 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 0.80 (m, 1 H, 6a-H), 0.91 (dd, J = 4.8, 4.8 Hz, 1 H, 6b-H), 1.84−2.11 (m, 5 H), 2.19 (ddt, J = 15.3, 6.9, 1.2 Hz, 1 H, 1′a-H), 2.45 (dd, 15.0, 6.7 Hz, 1 H, 1′b-H), 4.88−4.97 (m, 2 H, 3′-H), 5.67 (ddt, J = 17.6, 9.5, 6.9 Hz, 1 H, 2′-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.2 (CH_2, C-6), 21.6 (CH_2), 26.6 (CH), 31.0 (CH_2), 32.4 (CH_2), 36.4 (Cq), 116.4 (CH_2, C-3′), 134.8 (CH, C-2′), 214.9 (Cq); MS (70 eV) m/z 137 (M^+ + 1, 5), 136 (M^+, 14), 79 (100), 77 (35), 67 (38), 41 (42), 39 (92).

1-(But-3′-enyl)bicyclo[4.1.0]heptan-5-one (31). The cyclopropanization reaction (procedure A) of 3.80 g (25.0 mmol) of 3-(but-3′-enyl)cyclohexenone (**29**) yielded 1.89 g (46%) of **31** after chromatography on silica (eluent: ch/ee 9:1): IR (neat) 3060 cm^{-1}, 2905, 2815, 1675 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (dd, J = 10.5, 5.4 Hz, 1 H, 7-H *exo*), 1.39 (dd, J = 5.4, 5.5 Hz, 1 H, 7-H *endo*), 1.42−1.83 (m, 3 H), 1.93−2.09 (m, 3 H), 2.12−2.38 (m, 5 H), 4.95 (m, 1 H, 4′-H), 5.01 (ddt, J = 18.0, 2.0, 2.0, 1 H, 4′-H *trans*), 5.79 (ddt, J = 17.5, 10.5, 7.0 Hz, 1 H, 3′-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.3 (CH_2), 18.5 (CH_2), 25.7 (CH_2), 28.1 (Cq, C-1), 30.8 (CH_2), 33.7 (CH), 36.3 (CH_2), 38.5 (CH_2), 114.9 (CH_2, C-4′), 138.3 (CH, C-3′), 209.1 (Cq); MS (70 eV) m/z 164 (M^+, 10), 110 (100), 95 (78), 93 (58), 91 (40), 79 (84), 55 (80), 39 (34).

1-(Pent-4′-enyl)bicyclo[4.1.0]heptan-5-one (32). The cyclopropanization reaction (procedure A) of 4.10 g (25.0 mmol) of 3-(pent-4′enyl)cyclohexenone (**30**) yielded 3.10 g (70%) of **32** after chromatography on silica (eluent: ch/ee 9:1): IR (neat) 3060 cm^{-1}, 2910, 2840, 1675 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (dd, J = 10.5, 5.4 Hz, 1 H, 7-H *exo*), 1.38 (dd, J = 5.4, 5.5 Hz, 1 H, 7-H *endo*), 1.45−1.83 (m, 7 H), 1.91−2.12 (m, 4 H), 2.19−2.38 (m, 2 H), 4.95 (m, 1 H, 5′-H), 5.00 (ddt, J = 18.0, 2.0, 2.0 Hz, 1 H, 5′-H *trans*), 5.79 (ddt, J = 18.0, 10.5, 7.0 Hz, 1 H, 4′-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.4 (CH_2), 18.6 (CH_2), 23.6 (Cq), 25.8 (CH_2), 33.4 (CH_2), 33.8 (CH), 36.8 (CH_2), 37.5 (CH_2), 38.6 (CH_2), 114.9 (CH_2, C-5′), 138.6 (CH, C-4′), 209.4 (Cq); MS (70 eV) m/z 178 (M^+, 5), 135 (30), 110 (72), 107 (32), 95 (52), 94 (42), 93 (69), 81 (76), 79 (90), 68 (81), 67 (100), 55 (76), 39 (37). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.61; H, 10.38.

5-Methyl-1-(pent-2′-enyl)bicyclo[3.1.0]hexan-2-one (28). The cyclopropanization reaction (procedure A) of 3.30 g (20.0 mmol) of *cis*-jasmone (**27**) yielded 1.93 g (54%) of **28** after chromatography on silica (eluent: ch/ee 93:7): IR (neat) 3050 cm^{-1}, 2960, 2860, 1715 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 0.84 (d, J = 5.0 Hz, 1 H, 6a-H), 0.97 (t, J = 7.5 Hz, 3 H, 5′-H), 1.09 (d, J = 5.0 Hz, 1 H, 6b-H), 1.32 (s, 3 H, 12-H), 1.76−1.90 (m, 1 H), 1.95−2.23 (m, 6 H), 2.47 (dd, J = 16.0, 6.7 Hz, 1 H), 5.25−5.45 (m, 2 H, 2′-H, 3′-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (CH_3), 18.8 (CH_3), 20.3 (CH_2), 23.5 (CH_2), 24.5 (CH_2), 25.6 (CH_2), 28.8 (CH_2), 32.4 (Cq), 41.3 (Cq), 126.1 (CH), 132.2 (CH), 214.9 (Cq); MS (70 eV) m/z 179 (M^+ + 1, 10), 178 (M^+, 48), 149 (100), 121 (25), 107 (22), 93 (26), 79 (22), 55 (20).

Bicyclo[2.2.2]oct-5-en-2-one (Precursor of 3). A solution of 4.5 g (26 mmol) of 5-chloro-5-cyanobicyclo[2.2.2]oct-2-ene in 30 mL of DMSO was heated with a mixture of 3.5 g of KOH in 2.5 mL of water at 60 °C. After 6 h, the reaction mixture was poured into 50 mL of ice water and extracted four times with 50 mL portions of pentane. The combined organic layers were dried over Na_2SO_4. Two and a half grams (79%) of the ketone was obtained after chromatography on silica (eluent: ch/ee 9:1): IR (KBr) 3040 cm^{-1}, 2950, 2860, 1700 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 1.10−2.05 (m, 6 H), 2.92 (m, 1 H), 3.07 (m, 1 H), 6.13 (ddd, J = 7.8, 6.4, 1.4 Hz, 1 H), 6.41 (ddd, J = 8.1, 6.7, 1.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8 (CH_2), 24.6 (CH_2), 32.2 (CH), 40.3 (CH_2), 48.4 (CH), 128.3 (CH), 136.9 (CH), 212.8 (Cq); MS (70 eV) m/z 123 (M^+ + 1, 5), 122 (M^+, 4), 80 (74), 79 (100), 77 (22), 39 (35). Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.59; H, 7.89.

Tricyclo[3.3.0.0^{2,8}]octan-3-one (3). A solution of 1.0 g (40.5 mmol) of bicyclo[2.2.2]oct-5-en-2-one in 60 mL of acetone was degassed with argon and distributed among five quartz irradiation tubes. After 24 h of irradiation at 300 nm, the reaction was stopped, the solvent was removed under reduced pressure, and the product was obtained after chromatography on silica (eluent: ch/ee 85:5) in 68% yield: IR (neat) 3030 cm^{-1}, 2930, 2860, 1710 (s, C=O); ^1H NMR (360 MHz, $CDCl_3$) δ 1.42−1.56 (m, 2 H), 1.61 (d, J = 18.0 Hz, 1 H, 4a-H), 1.83 (dd, J = 9.1, 5.0 Hz, 1 H, 2-H), 1.87−2.06 (m, 3 H), 2.42 (dd, J = 18.1, 9.9 Hz, 1 H, 4b-H), 2.63 (ddd, J = 5.6, 5.5, 5.1 Hz, 1 H, 1-H), 2.85 (m, 1 H, 5-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.6 (CH_2), 30.8 (CH), 36.3 (CH), 37.4 (CH), 38.9 (CH), 40.8 (CH_2), 46.9 (CH_2), 216.1 (Cq); MS (70 eV) m/z 123 (M^+ + 1, 45), 122 (M^+, 6), 80 (100), 79 (38), 53 (23), 39 (66); UV (acetonitrile) λ_{max}= 208 nm (ϵ_{max}= 18 800), shoulder up to 310 nm.

5,6-Dicarboxy-8-(prop-2′enyl)bicyclo[2.2.2]octan-2-one (35). An LDA solution of 8.20 g of diisopropylamine, 100 mL of dry THF, and 36 mL of 1.6 M *n*-BuLi was prepared. At −78 °C, a solution of 6.70 g (49.2 mmol) of **12** in 15 mL of dry THF was added using the septum syringe technique. After the solution was stirred for 1 h at −78 °C, TMSCl was added dropwise. The solution was warmed to room temperature and stirred for an additional hour, and the solvent was removed at reduced pressure. Pentane was added to the crude reaction mixture, and the insoluble lithium salts were filtered off. Again, the solvent was evaporated under reduced pressure. The NMR spectrum of this crude reaction mixture showed a clean formation of the desired silyl enol ether **33**. The crude reaction product was used without further purification and was stirred with 6.02 g (60.8 mmol) of powdered maleic anhydride for 4 h without any solvent. Hydrolysis of the silyl enol ether and the anhydride was performed in one step. The material was treated with 40 mL of water and 2 mL of 2 M HCl for 30 min, and then solid sodium carbonate was added until a pH of 9−10 was reached. This solution was refluxed for 5 h, cooled to room temperature, and acidified with 2 M HCl. The solution was extracted with ether. The combined organic layers were dried over $MgSO_4$. After removal of the magnesium sulfate, the ether was evaporated under reduced pressure. Chloroform

was added until the solid dissolved. **35** (7.1 g, 57%) was obtained at 0 °C as a solid material: IR (KBr) 3200−2800 cm^{-1} (s), 1680 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 1.42 (ddd, J = 14.1, 4.5, 2.8 Hz, 1 H), 1.84 (m, 1 H), 1.98−2.11 (m, 3 H), 2.28−2.47 (m, 2 H), 2.55−2.71 (m, 2 H), 3.06 (brd, J = 11.2 Hz, 1 H), 3.28 (dd, J = 11.2, 2.6 Hz, 1 H), 5.02 (m, 2 H, 3′-H), 5.66 (ddt, J = 17.6, 9.8, 6.7 Hz, 1 H, 2′-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.8 (CH_2), 33.8 (CH), 35.3 (CH), 36.3 (CH_2), 39.3 (CH_2), 44.9 (CH), 45.4 (CH), 45.8 (CH), 117.2 (CH_2, C-3′), 135.3 (CH, C-2′), 178.1, 179.0 (Cq, COOH), 212.1 (Cq).

8-(Prop-2′-enyl)bicyclo[2.2.2]oct-5-en-2-one (36). A dry flask was filled with 50 mL of dry pyridine, and oxygen was bubbled through it for 15 min. After addition of 800 mg (3.17 mmol) of **35** and 1.90 g (4.3 mmol) of lead tetraacetate, the oxygen flow was kept over the solution and the flask was immersed in an oil bath (85 °C). Evolution of gas was observed immediately which ceased after 2 min. After an additional 5 min of heating, the mixture was cooled and poured into 10% nitric acid. Extraction with ether, followed by washing the combined organic layers with saturated sodium bicarbonate solution and drying over magnesium sulfate, yielded 130 mg (25%) of **36** after chromatography on silica (eluent: ch/ee 85:15): IR (neat) 3020 cm^{-1}, 2890, 1705 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 1.33 (dddd, J = 12.8, 5.2, 1.8, 0.7 Hz, 1 H, 7a-H), 1.79 (m, 1 H, 8-H), 1.89 (dddd, J = 12.8, 10.6, 3.7, 0.4 Hz, 1 H, 7b-H), 1.95 (dddd, J = 18.8, 3.5, 1.7, 0.4 Hz, 1 H, 3a-H), 2.09 (ddddd, J = 14.2, 7.2, 7.1, 1.3, 1.1 Hz, 1 H, 1′a-H), 2.21 (ddddd, J = 14.1, 7.6, 6.6, 1.3, 1.1 Hz, 1 H, 1′b-H), 2.27 (ddd, J = 18.8, 2.3, 0.8 Hz, 1 H, 3b-H), 2.79 (ddddd, J = 6.8, 3.5, 1.9, 1.7, 1.7 Hz, 1 H, 4-H), 3.07 (dddd, J = 6.5, 3.4, 1.6, 1.5 Hz, 1 H, 1-H), 5.02 (dddd, J = 10.1, 2.0, 1.1, 1.1 Hz, 1 H, 3′-H *cis*), 5.05 (dddd, J = 17.0, 2.0, 1.5, 1.5 Hz, 1 H, 3′-H *trans*), 5.77 (dddd, J = 17.1, 10.1, 7.3, 6.4 Hz, 1 H, 2′-H), 6.15 (ddddd, J = 8.0, 6.5, 1.6, 0.8, 0.8 Hz, 1 H, 6-H), 6.58 (ddd, J = 8.0, 6.6, 1.3 Hz, 1 H, 5-H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 29.6 (CH_2, C-7), 34.4 (CH_2, C-3), 34.8 (CH, C-8), 36.0 (CH, C-4), 38.4 (CH_2, C-1′), 48.9 (CH, C-1), 116.1 (CH_2, C-3′), 127.6 (CH, C-6), 136.6 (CH, C-2′), 139.0 (CH, C-5), 212.6 (Cq, C-2); MS (70 eV) m/z 162 (M^+, 5), 79 (100), 78 (48), 77 (31), 39 (32). An electrochemical bisdecarboxylation of 900 mg (3.57 mmol) of **35** (solvent: 60 mL of pyridine, 0.81 mL of TEA, 8.5 mL of water, and 20 mg of 2,6 di-*tert*-butylphenol) at carbon electrodes (2 × 4 cm, 200 V, 80 mA) gave the same product **36** in only 5% yield.

6-(Prop-2′-enyl)tricyclo[3.3.0.0^{2,8}]octan-3-one (37). A solution of 120 mg (0.74 mmol) of **36** in 12 mL of acetone was degassed with argon and irradiated in a Rayonet photoreactor at 300 nm using a quartz irradiation tube. After 3 h, the starting material was completely converted and the solvent was evaporated under reduced pressure. Compound **37** was the only product and could be isolated after chromatography on silica (eluent: ch/ee 85:15) in 58% yield: IR (neat) 3030 cm^{-1}, 2930, 2900, 2840, 1710 (s, C=O); ^1H NMR (360 MHz, $CDCl_3$) δ 1.15 (ddd, J = 13.7, 11.2, 2.0 Hz, 1 H, 7a-H), 1.82−2.13 (m, 6 H), 2.23 (dd, J = 18.3, 9.3 Hz, 1 H, 4b-H), 2.42 (ddddd, J = 11.2, 8.3, 8.1, 8.1, 5.3 Hz, 1 H, 6-H), 2.68 (ddd, J = 6.0, 5.2, 5.1 Hz, 1 H, 1-H), 2.78 (ddd, J = 9.4, 5.2, 5.2 Hz, 1 H, 5-H), 4.87−4.98 (m, 2 H, 3′-H), 5.66 (ddt, J = 17.0, 10.1, 6.9 Hz, 1 H, 2′-H); ^1H NMR (300 MHz, $CDCl_3/C_6D_6$ 1:1) δ 1.21 (ddd, J = 13.7, 11.2, 2.0 Hz, 1 H, 7a-H), 1.85 (dddd, J = 9.4, 6.6, 6.0, 2.0 Hz, 1 H, 8-H), 1.92 (dd, J = 9.4, 5.1 Hz, 1 H, 2-H), 2.05 (dd, J = 18.3, 0.9 Hz, 1 H, 4a-H), 2.00−2.10 (m, 2 H, 9-H), 2.11 (ddd, J = 13.7, 8.3, 6.6 Hz, 1 H, 7b-H), 2.22 (dd, J = 18.3, 9.5 Hz, 1 H, 4b-H), 2.42 (ddddd, J = 11.2, 8.3, 8.1, 8.1, 5.3 Hz, 1 H, 6-H), 2.61 (ddd, J = 6.0, 5.1, 5.1 Hz, 1 H, 1-H), 2.72 (dddd, J = 9.5, 5.3, 5.1, 0.9 Hz, 1 H, 5-H), 4.90−5.10 (m, 2 H, 3′-H), 5.73 (ddt, J = 17.0, 10.1, 6.9 Hz, 1 H, 2′-H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 28.5 (CH, C-8), 30.4 (CH_2, C-7), 34.6 (CH_2, C-9), 36.5 (CH, C-1), 37.3 (CH, C-2), 40.0 (CH, C-5), 40.2 (CH_2, C-4), 51.5 (CH, C-6), 115.4 (CH_2, C-3′), 136.8 (CH, C-2′), 216.5 (Cq, C-3); MS (70 eV) m/z 163 ($M^+ + 1$, 31) 162 (M^+, 5), 91 (88), 79 (65), 78 (66), 39 (100), calcd for $C_{11}H_{14}O$ 162.1044, found 162.1048.

1-(Pent-2′-enyl)-5-methyl-6-oxabicyclo[3.1.0]hexan-2-one (49). The epoxidation reaction (procedure B) of 1.15 g (7.0 mmol) of *cis*-jasmone (**27**) yielded 600 mg (47%) of **49** after chromatography on silica (eluent: pe/e 8:2): IR (neat) 3000 cm^{-1}, 2940, 2850, 1725 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, J = 7.6 Hz, 3 H, 5′-H), 1.50 (s, 3 H, 12-H), 1.95−2.48 (m, 7 H), 2.65 (dd, J = 14.5, 5.5 Hz, 1 H), 5.28 (m, 1 H), 5.45 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9 (CH_3), 16.5 (CH_3), 20.7 (CH_2), 21.8 (CH_2), 27.6 (CH_2), 31.9 (CH_2), 67.0 (Cq), 69.4 (Cq), 121.8 (CH), 135.1 (CH), 211.3 (Cq); MS (70 eV) m/z 181 ($M^+ + 1$, 4), 180 (M^+, 10), 109 (23), 99 (100), 81 (45), 71 (27), 69 (48), 55 (23), 43 (51), 41 (58), 39 (69); UV (acetonitrile) λ_{max} = 206 nm (ϵ_{max}= 11 250), λ = 294 nm (ϵ = 59). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.97; H, 8.79.

Photoproducts. 3,3-Dimethylcyclopentanone (4). The photolysis of 300 mg (2.72 mmol) of **1** and 2.72 g (27.2 mmol) of TEA in 13 mL of dry acetonitrile was performed according to procedure C. Due to the high volatility of the product **4**, a modified workup was used. The acetonitrile was not directly removed under reduced pressure, but ether was added and the solution was washed several times with water. The ether was cautiously evaporated from the organic layer, and the crude solution (3−4 mL) was subjected to chromatography on silica (eluent: pe/e 7:3). One hundred and twenty milligrams (39%) of **4** was isolated by this procedure: IR (neat) 2940 (s) cm^{-1}, 2860, 1735 (s, C=O), 1455, 1440, 1365, 1135, 875; ^1H NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 6 H, CH_3), 1.78 (t, J = 7.8 Hz, 2 H, 4-H), 2.05 (s, 2 H, 2-H), 2.31 (t, 2 H, 5-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.8 (CH_3, C-6), 36.4 (Cq, C-3), 37.2 (CH_2), 37.6 (CH_2), 53.6 (CH_2, C-5), 212.2 (Cq, C-1); MS (70 eV) m/z 112 (M^+, 8), 111 (8), 97 (70), 95 (45), 94 (45), 79 (70), 70 (68), 67 (92), 55 (52), 44 (80), 41 (60), 39 (100). Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.70; H, 10.95.

3,3-Dimethylcyclohexanone (5). The reaction of 655 mg (5.28 mmol) of **2** and 560 mg (5.54 mmol) of TEA in 24 mL of dry acetonitrile (procedure C) yielded 319 mg (48%) of **5** after chromatography on silica (eluent: ch/ee 93:7): IR (neat) 2920 (s) cm^{-1}, 2850, 1700 (s, C=O), 1440, 1360, 1285, 1215, 1070; ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (s, 6 H, CH_3), 1.59 (t, J = 6.0 Hz, 2 H, 4-H), 1.88 (m, 2 H, 5-H), 2.15 (s, 2 H, 2-H), 2.26 (t, J = 7.0 Hz, 2 H, 6-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.5 (CH_2, C-5), 28.8 (CH_3), 36.2 (Cq, C-3), 38.2 (CH_2, C-4), 41.0 (CH_2, C-2), 55.1 (CH_2, C-6), 212.2 (Cq, C-1); MS (70 eV) m/z 126 (M^+, 4), 125 (8), 110 (8), 83 (100), 82 (10), 69 (20), 55 (40), 41 (30), 39 (42). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.94; H, 11.16.

8-Methylbicyclo[4.3.0]nonan-3-one (38). The PET reaction (procedure C) of 600 mg (4.0 mmol) of **14** (6:1 mixture) and 1.0 g (10.0 mmol) of TEA in 24 mL of dry acetonitrile provided 40 mg of starting material and 130 mg of **38** (9:1 mixture) after purification using HPLC (eluent: ch/ee 9:1) in 23% yield based on conversion of **14**. The spectroscopic data refer to the main isomer: IR (neat) 2920 (s) cm^{-1}, 2840, 1700 (s, C=O); ^1H NMR (360 MHz, $CDCl_3$) δ 0.74 (ddd, J = 11.6, 11.6, 8.3 Hz, 1 H), 0.98 (d, J = 7.0 Hz, 3 H, 10-H), 1.30−1.55 (m, 3 H, 5a-H), 1.60 (m, 2 H, 1-H, 6-H), 1.95−2.13 (m, 3 H, 2a-H, 5b-H), 2.15−2.24 (m, 2 H, 4-H, 8-H), 2.35 (dddd, J = 14.9, 4.9, 2.3, 2.1 Hz, 1 H, 4a-H), 2.48 (ddd, J = 13.0, 2.3, 2.3 Hz, 1 H, 2b-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.1 (CH_3, C-10), 29.7 (CH_2, C-5), 32.5 (CH, C-8), 39.7 (CH_2), 40.1 (CH_2), 41.0 (CH_2, C-4), 45.8/46.3 (2 × CH, C-1/C-6), 47.4 (CH_2, C-2), 212.0 (Cq, C-3); MS (70 eV) m/z 153 ($M^+ + 1$, 8), 152 (M^+, 6), 134 (54), 109 (35), 108 (100), 95 (80), 81 (53), 67 (72), 55 (60), 43 (46), 41 (69), 39 (94). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.42; H, 10.69.

8-Methylbicyclo[4.3.0]nonan-2-one (40). The PET reaction (procedure C) of 200 mg (1.33 mmol) of **26** and 530 mg (5.3 mmol) of TEA in 12 mL of dry acetonitrile gave 30 mg of starting material and 60 mg of **40** (2:1 mixture) after chromatography on silica (eluent: pe/e 7:3) in 35% yield based on conversion of **26**. The spectroscopic data were taken from the mixture: IR (neat) 2920 (s) cm^{-1}, 2860, 1700 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) complex multiplet in the region of δ 1.2−2.7, the signals of two methyl groups of the two diastereoisomers could be assigned, main isomer δ 0.97 (J = 6.9 Hz), minor isomer δ 1.03 (J = 6.2 Hz, the integrals of these signals were used to determine the relative ratio of the two isomers); ^{13}C NMR (75 MHz, $CDCl_3$) main isomer δ 22.2 (CH_3), 23.9 (CH_2), 27.9 (CH_2), 31.5 (CH), 36.0 (CH_2), 40.0 (CH_2), 40.9 (CH_2), 42.5 (CH), 53.1 (CH), 214.7 (Cq, C-2); ^{13}C NMR (75 MHz, $CDCl_3$) minor isomer δ 21.0 (CH_3), 23.1 (CH_2), 28.5 (CH_2), 33.7 (CH),

35.1 (CH_2), 40.6 (CH_2), 41.3 (CH_2), 42.8 (CH), 53.1 (CH), 214.7 (Cq, C-2); MS (70 eV) *m/z* 153 ($M^+ + 1$, 10), 152 (M^+, 50), 109 (41), 97 (40), 93 (34), 81 (100), 79 (25), 67 (45), 55 (28), 41 (48), 39 (82).

Bicyclo[4.3.0]nonan-8-one (39). The PET reaction (procedure C) of 100 mg (0.73 mmol) of **13** (9:1 mixture) and 370 mg (3.67 mmol) of TEA in 12 mL of dry acetonitrile yielded 20 mg (20%) of **39** after chromatography on silica (eluent: pe/e 8:2): IR (neat) 2910 (s) cm^{-1}, 2840, 1735 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 1.11−1.25 (m, 2 H), 1.37 (m, 2 H), 1.57−1.65 (m, 2 H), 1.78−1.87 (m, 4 H), 1.96 (m, 2 H), 2.33 (dd, J = 16.7, 6.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3 (CH_2), 31.8 (CH_2), 43.9 (CH, C-1, C-6), 45.6 (CH_2, C-7, C-9), 218.2 (Cq); MS (70 eV) *m/z* 139 ($M^+ + 1$, 4), 138 (M^+, 10), 137 (32), 109 (28), 96 (21), 95 (32), 94 (100), 81 (78), 67 (82), 54 (28), 41 (52), 39 (92). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.78; H, 10.82.

2-Methylspiro[4.5]decan-7-one (41). The PET reaction (procedure C) of 850 mg (5.2 mmol) of **31** and 1.31 g (13.0 mmol) of TEA in 24 mL of dry acetonitrile yielded 352 mg of **41** (2:1 mixture) after purification using HPLC (eluent: ch/ee 85:15). The spectroscopic data were taken from the mixture: IR (neat) 2930 (s) cm^{-1}, 2860, 1710 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) signals in the region of δ 0.96−2.30, the methyl proton signals were well separated, main isomer δ 0.97 (J = 7.0 Hz), minor isomer δ 0.98 (J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) main isomer δ 20.7 (CH_3), 23.8 (CH_2), 33.4 (CH, C-2), 33.7 (CH_2), 38.3 (CH_2), 41.2 (CH_2), 47.2 (CH_2), 47.7 (Cq), 53.8 (CH_2), 54.9 (CH_2), 211.9 (Cq); MS (70 eV) *m/z* 166 (M^+, 30), 148 (18), 133 (24), 123 (100), 108 (28), 95 (38), 93 (28), 81 (52), 79 (24), 67 (60), 55 (36), 39 (59).

8-Methylspiro[5.5]undecan-2-one (42). The PET reaction (procedure C) of 940 mg (5.28 mmol) of **32** and 1.31 g (13.0 mmol) of TEA in 24 mL of dry acetonitrile yielded 60 mg of **42** (3:1 mixture) after purification using HPLC (eluent: ch/ee 93:7): The spectroscopic data were taken from the mixture: IR (neat) 2940−2820 (s) cm^{-1}, 1695 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) all signals were in the region of δ 0.82−2.30; ^{13}C NMR (75 MHz, $CDCl_3$) main isomer δ 14.5 (CH_3), 21.6 (CH_2), 32.4 (CH_2), 35.3 (CH_2), 36.0 (CH_2), 36.6 (CH_2), 39.3 (Cq), 40.4 (CH_2), 41.4 (CH_2), 44.1 (CH), 49.2 (CH_2), 213.2 (Cq); MS (70 eV) *m/z* 180 (M^+, 24), 162 (27), 147 (15), 137 (100), 122 (47), 110 (38), 95 (69), 93 (32), 81 (45), 67 (57), 55 (47), 41 (62), 39 (68).

1-Methyl-3-propylbicyclo[3.3.0]octan-6-one (43). The PET reaction (procedure C) of 810 mg (4.55 mmol) of **28** and 1.80 g (18.0 mmol) of TEA in 24 mL of dry acetonitrile yielded 320 mg of starting material, 70 mg (17% based on conversion of **28**) of **43**, and 180 mg (34% based on conversion of **28**) of the oxetanes **45** and **46** after purification using HPLC (eluent: ch/ee 93:7): IR (neat) 2951 cm^{-1}, 2926, 2864, 1739 (s, C=O); ^1H NMR (360 MHz, $CDCl_3$) δ 0.84 (m, 3 H, 3′-H), 1.18−1.30 (m, 8 H), 1.45 (ddd, J = 12.8, 11.1, 10.1 Hz, 1 H, 4a-H), 1.70−1.84 (m, 4 H), 2.03 (m, 1 H, 4b-H), 2.11 (dm, J = 10.1 Hz, 1 H, 5-H), 2.24 (dddd, J = 18.0, 8.2, 5.7, 0.8 Hz, 1 H, 7a-H), 2.40 (dddd, J = 18.0, 9.4, 9.4, 1.6 Hz, 1 H, 7b-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6 (CH_3, C-3′), 22.0 (CH_2, C-2′), 28.9 (CH_3, C-12), 35.4 (CH_2, C-8), 37.1 (CH_2, C-2 or C-4), 38.3 (CH_2, C-1′), 39.2 (CH_2, C-7), 40.3 (CH, C-3), 47.2 (Cq, C-1), 48.9 (CH_2, C-2 oder C-4), 59.4 (CH, C-5), 223.4 (Cq, C-6); MS (70 eV) *m/z* 181 ($M^+ + 1$, 10), 180 (M^+, 2), 97 (100), 95 (12), 81 (42), 67 (14), 55 (10), 39 (20), calcd for $C_{12}H_{20}O$ 180.1514, found 180.1517. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.53; H, 11.06.

3-Ethyl-8-methyl-2-oxatetracyclo[4.4.0.0^{1,4}.0^{6,8}]-decane (45). IR (neat) 2980−2920 (s) cm^{-1}, 1460, 1440, 1380, 1320, 1285, 1240, 1185, 1130, 1110, 1095,1080, 1035, 1020, 1005, 970, 930, 905, 890, 850; ^1H NMR (360 MHz, $CDCl_3$) δ 0.61 (d, J = 5.7 Hz, 1 H, 7a H), 0.90 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 0.92 (d, J = 5.7 Hz, 1 H, 7b-H), 1.08 (s, 3 H, CH_3), 1.46 (ddd, J = 15.0, 9.3, 9.3 Hz, 1 H, 10a-H), 1.50−1.80 (m, 3 H, 11-H, 9a-H), 1.88 (ddd, J = 13.3, 9.5, 2.0 Hz, 1 H, 9b-H), 2.09 (ddd, J = 15.0, 9.5, 2.3 Hz, 1 H, 10b-H), 2.25 (dd, J = 12.0, 6.5 Hz, 1 H, 5a-H), 2.44 (dd, J = 12.0, 3.0 Hz, 1 H, 5b-H), 2.90 (ddd, J = 6.4, 2.1, 2.1 Hz, 1 H, 4-H), 4.42 (ddd, J = 6.4, 6.4, 2.1 Hz, 1 H, 3-H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 8.4 (CH_3, C-12), 19.6 (CH_2, C-7), 20.4 (CH_3, C-13), 28.0 (CH_2, C-5), 28.3 (Cq, C-8), 30.3 (CH_2, C-11), 32.6 (CH_2), 33.1 (CH_2), 44.1 (CH, C-4), 44.6 (Cq, C-6), 87.5 (CH, C-3), 102.4 (Cq, C-1); MS (70 eV) *m/z* 179 ($M^+ + 1$, 20), 163 (32), 161 (65), 149 (100), 131 (32), 121 (38), 107 (41), 105 (72), 95 (34), 93 (48), 91 (53), 81 (42), 79 (47), 67 (31), 55 (35), 53 (22), 41 (52), 39 (88), calcd for $C_{12}H_{18}O$ 178.1358, found 178.1359.

Bicyclo[3.3.0]octan-3-one (6). The PET reaction (procedure C) of 122 mg (1.0 mmol) of **3** and 505 mg (5.0 mmol) of TEA in 12 mL of dry acetonitrile yielded 45 mg (26%) of **6** after chromatography on silica (eluent: pe/e 8:2): IR (neat) 2920 cm^{-1}, 2840, 2820, 1720 (s, C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 1.32−1.42 (m, 2 H), 1.55−1.81 (m, 2 H), 1.86−2.01 (m, 4 H), 2.35−2.49 (m, 2 H), 2.65 (m, 2 H, 1-H, 5-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.5 (CH_2), 33.5 (CH_2), 39.6 (CH, C-1, C-5), 44.6 (CH_2, C-2, C-4), 221.1 (Cq, C-3); MS (70 eV) *m/z* 125 ($M^+ + 1$, 8), 124 (M^+, 6), 109 (5), 81 (30), 80 (32), 67 (100), 55 (20), 54 (22), 41 (26), 39 (52). Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.14; H, 9.55.

8-Methyltricyclo[5.2.1^{1,7}.0^{2,6}]decane-4-one (44). The PET reaction (procedure C) of 150 mg (0.92 mmol) of **37** and 1.01 g (10.0 mmol) of TEA in 12 mL of dry acetonitrile yielded 40 mg (27%) of **44** after chromatography on silica (eluent: ch/ee 85:15): IR (neat) 2900 cm^{-1}, 2840, 1725 (s, C=O), 1440, 1365, 1160, 1060, 905; ^1H NMR (360 MHz, C_6D_6) δ 0.58 (dddd, J = 12.1, 7.9, 4.3, 1.5 Hz, 1 H, 9a-H), 0.68 (d, J = 6.1 Hz, 3 H, 11-H), 1.06 (ddddd, J = 9.8, 1.7, 1.7, 1.7, 1.5 Hz, 1 H, 10a-H), 1.36 (ddd, J = 9.8, 1.7, 1.5 Hz, 1 H, 10b-H), 1.41−1.48 (m, 2 H, 8-H, 9b-H), 1.58 (m, 1 H, 7-H), 1.80−1.98 (m, 5 H), 2.05−2.18 (m, 2H, 2-H, 6-H); ^{13}C NMR (90 MHz, C_6D_6) δ 22.3 (q, J(CH) = 128.8 Hz, C-11), 27.9 (d, J(CH) = 125.5 Hz, C-8), 32.5 (t, J(CH) = 125.5 Hz, C-9), 37.4 (t, J(CH) = 126.0 Hz, C-10), 37.6 (d, J(CH) = 137.6 Hz, C-2), 38.8 (t, J(CH) = 124.8 Hz, C-3/C-5), 39.2 (d, J(CH) = 140.8 Hz, C-6), 42.0 (d, J(CH) = 140.8 Hz, C-1), 48.2 (d, J(CH) = 136.6 Hz, C-7), 217.5 (s, C-4); MS (70 eV) *m/z* 165 ($M^+ + 1$, 18), 164 (M^+, 10), 149 (8), 133 (6), 121 (16), 107 (35), 94 (37), 93 (49), 91 (32), 83 (74), 81 (92), 80 (100), 79 (50), 67 (48), 65 (21), 55 (13), 53 (24), 41 (31), 39 (83).

Photolysis of *cis*-Epoxyjasmone (49). The PET reaction (procedure C) of 150 mg (0.8 mmol) of **49** and 420 mg (4.1 mmol) of TEA in 12 mL of dry acetonitrile yielded 20 mg (15%) of *cis*-jasmone (**27**) after chromatography on silica (eluent: pe/e 9:1). The spectroscopic data were identical with those of the commercially available material.

Reactions with *N*-Silylated Amines. 3,3-Dimethyl-1-[(trimethylsilyl)oxy]cyclohexane (51). Irradiation (procedure D) of 124 mg (1.0 mmol) of **2** and 117 mg (1.0 mmol) of *N*,*N*-dimethyl(trimethylsilyl)amine in 12.0 mL of dry acetonitrile yielded 45 mg (22%) of **51** after chromatography on silica (eluent pe/e 9:1). The enol ether **50** was formed only in a very small amount detectable by GLC: IR (neat) 2910 cm^{-1}, 2840, 1450, 1355, 1240 (s), 1075 (s), 1030, 945, 925, 900, 875, 830 (s), 740; ^1H NMR (360 MHz, $CDCl_3$) δ 0.01 (s, 9 H, OTMS), 0.86 (s, 3 H, 7-H), 0.90 (s, 3 H, 7′-H), 1.04 (ddd, J = 13.1, 13.1, 4.2 Hz, 1 H, 4-H *axial*), 1.10 (dd, J = 12.4, 12.6 Hz, 1 H, 2-H *axial*), 1.13 (m, 1 H, 6-H *axial*), 1.25 (m, 1 H, 4-H *equatorial*), 1.38 (ddddd, J = 13.4, 13.4, 13.4, 3.6, 3.6 Hz, 1 H, 5-H *axial*), 1.52 (dddd, J = 12.6, 4.3, 2.1, 2.1 Hz, 1 H, 2-H), 1.58 (m, 1 H, 5-H), 1.78 (m, 1 H, 6-H *equatorial*), 2.96 (dddd, J = 11.7, 11.7, 4.3, 4.3 Hz, 1 H, 1-H *axial*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.0 (CH_3, OTMS), 20.9 (CH_2), 25.2 (CH_3), 32.0 (Cq, C-3), 32.9 (CH_3), 35.9 (CH_2), 38.3 (CH_2), 48.9 (CH_2), 68.4 (CH, C-1); MS (70 eV) *m/z* 185 (45), 157 (52), 129 (20), 95 (18), 75 (100), 73 (40), 55 (10), 45 (16), 41 (22). Anal. Calcd for $C_{11}H_{24}OSi$: C, 65.92; H, 12.07. Found: C, 65.72; H, 11.78.

3,3-Dimethyl-1-[(trimethylsilyl)oxy]cyclohex-1-ene (50). The irradiation (procedure D) of 340 mg (3.5 mmol) of **2** and 2.95 g (25.0 mmol) of *N*,*N*-dimethyl(trimethylsilyl)amine in 10.0 mL of dry acetonitrile yielded 230 mg (22 %) of **50** after chromatography on silica (eluent: pe/e 8:2). The silyl ether **51** was formed only in a very small amount detectable by GLC: IR (neat) 2930 cm^{-1}, 2840, 1650, 1355, 1245 (s), 1205, 1135, 1030, 960, 875, 835 (s), 745; ^1H NMR (360 MHz, $CDCl_3$) δ 0.12 (s, 9 H, OTMS), 0.95 (s, 6 H, 7-H), 1.30 (m, 2 H), 1.63 (m, 2 H, 5-H), 1.58 (dt, J = 1.4, 6.5 Hz, 2 H), 4.62 (br s, 1 H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.0 (CH_3, OTMS), 19.9

(CH_2), 29.8 (CH_2), 30.5 (CH_3, C-7), 31.7 (Cq, C-3), 36.9 (CH_2), 115.8 (CH, C-2), 148.7 (Cq, C-1); MS (70 eV) *m/z* 198 (M^+, 20), 183 (75), 170 (38), 155 (20), 127 (42), 115 (20), 75 (72), 73 (100), 55 (18), 45 (26), 40 (34). Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.59; H, 11.17. Found: C, 66.60; H, 11.18.

***cis*-1-(*N*,*N*-Dimethylacetamido)-2-methylcyclopentane (52).** The irradiation (procedure D) of 180 mg (1.47 mmol) of **3** and 176 mg (1.47 mmol) of *N*,*N*-dimethyl(trimethylsilyl)amine in 24.0 mL of dry acetonitrile yielded 80 mg (33%) of **52** after chromatography on Al_2O_3 (eluent: ch/ee 85:15): IR (neat) 2920 cm^{-1}, 2864, 1630 (s, C═ON), 1445, 1390, 1260, 1110; ^1H NMR (300 MHz, C_6D_6) δ 0.77 (d, J = 7.1 Hz, 3 H, CH_3), 1.21 (dddd, J = 10.2, 8.5, 5.7, 5.0 Hz, 1 H, 3a-H), 1.32 (dddd, J = 12.3, 9.3, 9.0, 7.1 Hz, 1 H, 5a-H), 1.49 (ddddd, J = 12.7, 9.5, 8.7, 7.1, 5.7 Hz, 1 H, 4a-H), 1.63 (ddddd, J = 12.7, 9.3, 8.5, 6.0 4.2 Hz, 1 H, 4b-H), 1.73 (dddd, J = 10.2, 9.5, 7.0, 6.0 Hz, 1 H, 3b-H), 1.87 (dddd, J = 12.3, 8.7, 6.6, 4.2 Hz, 1 H, 5b-H), 1.92 (dd, J = 15.5, 8.5 Hz, 1 H, 1′a-H), 2.09 (dd, J = 15.5, 6.6 Hz, 1 H, 1′b-H), 2.16 (dddq, J = 7.0, 7.0, 5.0, 7.1 Hz, 1 H, 2-H), 2.24 (s, 3 H, N−CH_3), 2.50 (ddddd, J = 9.0, 8.5, 7.0, 6.6, 6.6 Hz, 1 H, 1-H), 2.68 (s, 3 H, N−CH_3′); ^{13}C NMR (75 MHz, C_6D_6) δ 15.4 (CH_3), 22.7 (CH_2, C-4), 30.3 (CH_2, C-3), 33.3 (CH_2, C-5), 34.1 (CH_2, C-1′), 35.4 (N−CH_3), 36.1 (CH, C-2), 37.4 (N−CH_3′), 39.6 (CH, C-1), 173.1 (Cq, CON); MS (70 eV) *m/z* 170 (M^+ + 1, 100), 169 (M^+, 3), 154 (12), 126 (12), 87 (65), 72 (82), 55 (32), 45 (52), 44 (48), 39 (38).

***cis*-1-(*N*,*N*-Diethylacetamido)-2-methylcyclopentane (53).** The irradiation (procedure D) of 122 mg (1.0 mmol) of **3** and 145 mg (1.0 mmol) of *N*,*N*-diethyl(trimethylsilyl)amine in 12.0 mL of dry acetonitrile yielded 70 mg (35%) of **53** after chromatography on Al_2O_3 (eluent: ch/ee 85:15): IR (neat) 2920 cm^{-1}, 2850, 1625 (s, C═ON), 1415, 1370, 1240, 830; ^1H NMR (300 MHz, $CDCl_3$) δ 0.76 (d, J = 7.1 Hz, 3 H, CH_3), 1.03 (t, J = 7.1 Hz, 3 H, NCH_2CH_3), 1.11 (t, J = 7.1 Hz, 3 H, NCH_2CH_3′), 1.15−1.80 (m, 6 H), 2.00−2.16 (m, 2 H), 2.21−2.35 (m, 2 H), 3.26 (q, J = 7.1 Hz, 2 H, N−CH_2CH_3), 3.31 (dq, J = 7.1, 2.4 Hz, 2 H, N−CH_2′CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0 (CH_3), 14.4 (CH_3), 15.3 (CH_3), 22.6 (CH_2), 30.1 (CH_2), 33.4 (CH_2), 33.7 (CH_2), 35.9 (CH), 40.0 (CH), 41.9 (CH_2), 44.6 (CH_2), 173.1 (Cq, C-7); MS (70 eV) *m/z* 198 (M^+ + 1, 100), 197 (M^+, 3), 182 (12), 154 (12), 115 (82), 100 (100), 72 (48), 58 (72), 55 (45), 44 (46), 41 (42), 39 (32).

***N*,*N*-Dimethyl-2-acetyl-(*Z*)-hept-4-enoic Amide (55).** The irradiation (procedure D) of 360 mg (2.0 mmol) of **49** and 1.17 g (10.0 mmol) of *N*,*N*-dimethyl(trimethylsilyl)amine in 24.0 mL of dry acetonitrile yielded 150 mg (44%) of **55** after chromatography on Al_2O_3 (eluent: ch/ee 6:4): IR (neat) 2950 cm^{-1}, 2860, 1710 (s, C═O), 1620 (s, C═ON), 1395, 1250, 965; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 2.02 (m, 2 H, CH_2CH_3), 2.11 (s, 3 H, 2′-H), 2.60 (br t, J = 7.3 Hz, 2 H, 3-H), 2.96 (s, 3 H, N−CH_3), 3.02 (s, 3 H, N−CH_3′), 3.55 (t, J = 7.2 Hz, 1 H, 2-H), 5.18 (dtt, J = 10.9, 7.2, 1.5 Hz, 1 H, 4-H), 5.41 (dtt, J = 10.9, 7.1, 1.2 Hz, 1 H, 5-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (CH_3, C-7), 20.4 (CH_2), 26.8 (CH_3, C-2′), 27.0 (CH_2), 35.2 (N−CH_3), 36.9 (N−CH_3′), 57.8 (CH, C-2), 124.4 (CH), 134.3 (CH), 168.8 (Cq, C-1), 204.2 (Cq, C-1′); MS (70 eV) *m/z* 198 (M^+ + 1, 43), 197 (M^+, 5), 182 (4), 154 (100), 129 (12), 109 (24), 81 (21), 72 (81), 55 (10), 45 (21), 44 (32), 43 (47), 39 (23).

Intramolecular Oxetane Formations. Reaction of 5-Methyl-1-(pent-2′-enyl)bicyclo[3.1.0]hexan-2-one (28). A solution of 250 mg (1.4 mmol) of **28** in 12 mL of benzene was placed into a Pyrex irradiation tube and degassed with argon. The irradiation was performed in a Rayonet photoreactor using 300 nm lamps. After complete disappearance of the starting material, the reaction was stopped and the solvent was evaporated under reduced pressure. The NMR spectrum of the crude material showed a ratio of 3.2:1, **45**/**46** as the only products. The products were separated using HPLC (eluent: ch/ee 93:7). Ninety milligrams (36%) of pure **45** and 15 mg (6%) of pure **46** were isolated. Both compounds have a low boiling point and are quite unstable.

Main isomer 45: spectroscopic data identical with those of compound **45** isolated after the PET reaction.

Minor isomer 46: IR (neat) 2950 cm^{-1}, 2910 (s), 2840, 1450, 1430, 1370, 1280, 1105, 1085, 1030, 960, 930, 900, 880; ^1H NMR (300 MHz, $CDCl_3$) δ 0.45 (d, J = 5.7 Hz, 1 H, 7a-H), 0.75 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 0.77 (d, J = 5.7 Hz, 1 H, 7b-H), 0.96 (s, 3 H, 13-H), 1.28 (m, 1 H, 10a-H), 1.56 (m, 1 H, 9a-H), 1.65−1.84 (m, 3 H, 9b-H, 11-H), 1.89 (dd, J = 12.4, 7.1 Hz, 1 H, 5a-H), 2.11 (ddd, J = 14.8, 9.3, 2.1 Hz, 1 H, 10b-H), 2.52 (dd, J = 12.4, 3.1 Hz, 1 H, 5b-H), 3.08 (ddd, J = 6.4, 6.4, 3.3 Hz, 1 H, 4-H), 4.73 (ddd, J = 6.9, 6.9, 6.7 Hz, 1 H, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.8 (CH_3, C-12), 18.9 (CH_2, C-7), 20.1 (CH_3, C-13), 20.3 (CH_2), 24.6 (CH_2), 28.0 (Cq, C-8), 31.1 (CH_2), 32.5 (CH_2), 41.5 (CH, C-4), 43.9 (Cq, C-6), 82.1 (CH, C-3), 101.4 (Cq, C-1); MS (70 eV) *m/z* 179 (M^+ + 1, 16), no M^+, 163 (28), 161 (51), 149 (96), 131 (34), 121 (48), 107 (48), 105 (63), 95 (40), 93 (65), 91 (55), 81 (51), 79 (62), 67 (32), 55 (35), 53 (27), 41 (63), 39 (100).

Reaction of 1-(Prop-2′-enyl)bicyclo[3.1.0]hexan-2-one (25). A solution of 200 mg (1.5 mmol) of **25** in 12 mL of benzene was placed in a Pyrex irradiation tube and degassed with argon. The irradiation was performed in a Rayonet photoreactor using 300 nm lamps. After complete disappearance of the starting material, the reaction was stopped and the solvent was removed under reduced pressure. The NMR spectra of the crude material showed a ratio of 8:1 **47**/**48** as the only products. The products were separated using chromatography on silica (eluent: pe/e 7:3). One hundred milligrams (50%) of pure **47** and 10 mg (5%) of pure **48** were isolated. Both compounds have a low boiling point and are unstable, especially **48**.

Main isomer 47, (2-oxatetracyclo[4.4.0.0^{1,4}.0^{6,8}]decane): IR (neat) 2960 cm^{-1}, 2910 (s), 2850 (s), 1435, 1302, 1220, 1165, 1085, 1037, 1020, 960, 918, 750; ^1H NMR (300 MHz, $CDCl_3$) δ 0.79 (dd, J = 5.7, 5.7 Hz, 1 H, 7a-H), 0.97 (dd, J = 8.1, 5.7 Hz, 1 H, 7b-H), 1.23 (m, 1 H), 1.45 (ddd, J = 15.0, 8.8, 8.8 Hz, 1 H, 10a-H), 1.72 (dddd, J = 13.9, 9.3, 2.4, 0.7 Hz, 1 H, 9b-H), 2.03 (m, 1 H), 2.26 (ddd, J = 15.0, 9.8, 2.4 Hz, 1 H, 10b-H), 2.40 (ddd, J = 12.0, 5.3, 1.2 Hz, 1 H, 5a-H), 2.70 (dd, J = 12.1, 2.9 Hz, 1 H, 5b-H), 3.31 (m, 1 H, 4-H), 4.54 (dd, J = 6.2, 2.4 Hz, 1 H, 3a-H), 4.87 (ddd, J = 6.2, 6.2, 1.4 Hz, 1 H, 3b-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7 (CH_2, C-5), 25.8 (CH, C-4), 26.3 (CH_2), 31.8 (CH_2), 32.8 (CH_2), 39.3 (CH, C-8), 40.8 (Cq, C-6), 75.8 (CH_2, C-9), 106.3 (Cq, C-1).

Minor isomer 48, (9-oxatetracyclo[6.1.1.0.^{3,5}0.^{3,8}]decan): ^1H NMR (300 MHz, $CDCl_3$) δ 0.52 (dd, J = 5.3, 5.0 Hz, 1 H, 5a H), 0.81−0.93 (m, 1 H), 0.97 (dd, J = 8.3, 5.5 Hz, 1 H, 5b-H), 1.34 (ddd, J = 14.9, 9.3, 6.9 Hz, 1 H, 2a-H), 1.59−1.71 (m, 1 H, 3a-H), 2.09 (m, 1 H), 2.29 (ddd, J = 14.8, 10.3, 3.9 Hz, 1 H, 2b-H), 2.57 (dd, J = 13.1, 4.0 Hz, 1 H, 7a-H), 2.75 (d, J = 13.1 Hz, 1 H, 7b-H), 4.77 (d, J = 6.2 Hz, 1 H, 10a-H), 4.97 (dd, J = 6.2, 1.2 Hz, 1 H, 10b-H), 5.31 (br d, J = 4.0 Hz, 1 H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.0 (CH_2, C-5), 27.4 (CH, C-4), 29.3 (CH_2), 32.2 (CH_2), 37.5 (CH_2), 38.2 (Cq, C-6), 59.6 (Cq, C-1), 78.6 (CH_2, C-10), 88.5 (CH, C-8).

Reactions in the Presence of Methanol. 2-Acetyl-(*Z*)-hept-4-enoic acid methyl ester (54a). The irradiation (procedure D) of 180 mg (1.0 mmol) of **49** and 1.0 mL (24.0 mmol) of methanol in 12.0 mL of dry acetonitrile yielded 55 mg (29%) of **54a** and 20 mg (11%) of **56a** after chromatography on silica (eluent: ch/ee 85:15): IR (neat) 2950 cm^{-1}, 2860, 1790, 1730, 1705, 1430, 1350, 1165, 1120, 965; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 7.1 Hz, 3 H, CH_2CH_3), 1.90−2.07 (m, 2 H), 2.18 (s, 3 H, 2′-H), 2.42−2.65 (m, 2 H), 3.34 (m, 1 H), 3.70 (s, 3 H, OCH_3), 5.11−5.31 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7 (CH_3, C-7), 25.4 (CH_2), 29.1 (CH_3, C-2′), 31.4 (CH_2), 52.3 (CH_3, OCH_3), 59.7 (CH, C-2), 124.3 (CH), 135.5 (CH), 169.9 (Cq, C-1), 202.7 (Cq, C-1′); MS (70 eV) *m/z* 185 (M^+ + 1, 12), 184 (M^+, 28), 152 (8), 141 (30), 109 (32), 95 (29), 81 (72), 67 (27), 55 (15), 43 (100), 39 (33). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.30; H, 8.64.

1-Methyl-2-(methoxycarbonyl)-6-ethyl-5-oxabicyclo-[2.1.1]hexane (56a): IR (neat) 2960 cm^{-1}, 2910 (s), 2850 (s), 1435, 1302, 1220, 1165, 1085, 1037, 1020, 960, 918, 750; ^1H NMR (300 MHz, $CDCl_3$) δ 0.77 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 0.97−1.10 (m, 2 H, CH_2CH_3), 1.44 (s, 3 H, CH_3), 2.10 (dd, J = 12.0, 8.4 Hz, 1 H, 3a-H), 2.33 (ddt, J = 3.5, 1.4, 7.4 Hz, 1 H, 6-H), 2.39 (dddd, J = 11.9, 4.0, 2.6, 1.4 Hz, 1 H, 3b-H), 2.80 (dd, J = 8.6, 4.3 Hz, 1 H, 2-H), 3.68 (s, 3 H, OCH_3), 4.43 (dd, J = 3.3, 2.6 Hz, 1 H, 4-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.1

(CH_3, C-8), 17.8 (CH_3, C-9), 19.0 (CH_2, C-7), 32.6 (CH_2, C-3), 45.9 (CH), 51.7 (CH_3, C-11), 58.6 (CH), 81.1 (CH, C-4), 94.0 (Cq, C-1), 174.1 (Cq, C-10); MS (70 eV) *m*/*z* 184 (M^+, 8), 167 (6), 166 (42), 152 (12), 141 (34), 125 (48), 109 (48), 107 (34), 95 (49), 81 (68), 79 (22), 67 (37), 59 (12), 55 (46), 53 (27), 43 (100), 41 (47), 39 (62), calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1096.

2-Acetyl-(*Z*)-hept-4-enoic Acid Trideuteriomethyl Ester (54b). The irradiation (procedure D) of 180 mg (1.0 mmol) of **49** and 1.0 mL (24.0 mmol) of methanol-*d*-4 in 12.0 mL of dry acetonitrile yielded 66 mg (34%) of **54b** and 25 mg (13%) of **56b** after chromatography on silica (eluent: ch/ee 85:15): IR (neat) 2940 cm^{-1}, 2910, 2850, 1730 (s), 1700, 1450, 1345, 1215, 1075, 960; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.88−2.07 (m, 2 H), 2.18 (s, 3 H, 2′-H), 2.42−2.65 (m, 2 H), 3.42 (t, J = 7.4 Hz, 1 H, 2-H), 5.13−5.32 (m, 1 H), 5.35−5.54 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7 (CH_3, C-7), 25.4 (CH_2), 28.8 (CH_3, C-2′), 31.2 (CH_2), 59.4 (CH, C-2), 124.3 (CH), 134.8 (CH), 169.9 (Cq, C-1), 202.6 (Cq, C-2′); MS (70 eV) *m*/*z* 188 (M^+ + 1, 32), 187 (M^+, 57), 144 (38), 125 (12), 120 (12), 109 (50), 95 (41), 81 (91), 68 (29), 67 (28), 55 (14), 53 (16), 43 (100), 41 (26), 39 (41).

1-Methyl-2-deuterio-2-[(trideuteriomethoxy)carbonyl]-6-ethyl-5-oxabicyclo[2.1.1]hexane (56b): IR (neat) 2950 cm^{-1}, 2920, 2860, 1720, 1450, 1375, 1300, 1270, 1150, 1085, 965, 860, 840; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 0.97−1.11 (m, 2 H, CH_2CH_3), 1.42 (s, 3 H, 9-H), 2.07 (dt, J = 12.1, 1.4 Hz, 1 H, 3a-H), 2.30−2.43 (m, 2 H, 6-H, 3b-H), 4.43 (dd, J = 3.3, 2.4 Hz, 1 H, 4-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.1 (CH_3, C-8), 17.7 (CH_3, C-9), 18.9 (CH_2, C-7), 32.5 (CH_2, C-3), 45.9 (small signal, CD), 58.3 (CH, C-6), 81.1 (CH, C-4), 94.8 (Cq, C-1), 173.7 (Cq, C-10); MS (70 eV) *m*/*z* 188 (M^+, 20), 187 (21), 170 (100), 145 (53), 129 (87), 109 (67), 108 (91), 96 (80), 82 (52), 68 (29), 56 (18), 54 (23), 43 (71), 41 (32), 39 (58).

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