Chemical Oxidation of α,β-Amino Alcohols with Dioxygen Hexafluoroantimonate in CH_2Cl_2. α,β-Amino alcohols were weighed in a glovebox and transferred into a 5-mL Pyrex test tube which was sealed with a septum cap and parafilm. A molar equivalent amount of dioxygen hexafluoroantimonate was weighed separately and placed into a test tube with a T14/20 adaptor (microflask) containing a stirbar, which was capped with a high-vacuum T-switch stopcock. After the sample was removed from the glovebox, 1 mL of purified methylene chloride solvent was added to the α,β-amino alcohol solid by injection through the septum cap. The microflask was connected to the nitrogen gas line and cooled in a temperature bath to below −110 °C. The methylene chloride solution of amino alcohol was added to the cold O_2SbF_6 solid with a syringe under a nitrogen atmosphere. The solution immediately froze on the wall of the reaction cell. The cell was isolated from the N_2 line and thawed in a temperature bath (T = ca. −90 °C) with stirring. The reaction was performed at −85 °C for 2 h. After reaction the solvent was removed under vacuum at T = 30 °C. The vacuum was then released by slowly blowing nitrogen gas into the sample until atmospheric pressure was reached. CD_3CN or C_6D_6 was added to the reaction tube to dissolve the oxidation products, and the resulting solution was carefully pipeted into a NMR tube. An NMR spectrum was taken immediately after the sample was prepared.

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Novel [3 + 2] Photocycloadditions of 3-(1-Alkynyl)-2-cycloalken-1-ones with Alkenes†

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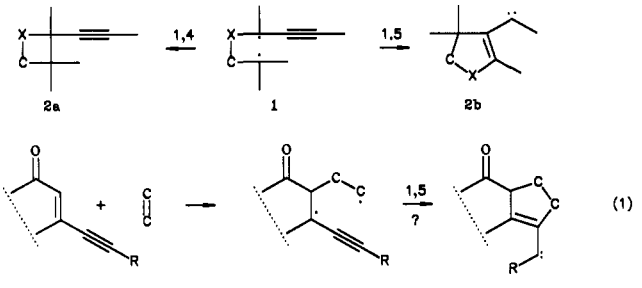
Abstract: Photochemical cycloaddition of 3-alkynylcycloalkenones **3a,b,c** and **4** with tetramethylethylene (**8**) at ~40 °C leads to mixtures of 1:1 adducts that arise largely from 1,5 closure of the biradical intermediate (eq 1), providing examples of a novel [3 + 2] cycloaddition reaction. Similar reactions occur between these same ketones and 1,1-dimethoxy-2-methylpropene (**9**) and 1,1-dimethoxyethylene (**10**). In several cases, these reactions lead in a single step to complex and otherwise difficultly accessible systems such as **21** and **30**. In contrast, at −60 °C, normal 1,4 closure is favored in addition of **4** with **8**. This and previously observed temperature effects on related rearrangements of triplet biradicals suggest that such biradical rearrangements occur prior to and in competition with intersystem crossing to the singlet.

Investigations over the past decade have demonstrated that alkyl propargyl 1,4-biradicals of general structure **1** (X = C, O), which may be created photochemically in several different ways, can either close 1,4 to form alkynyl-substituted four-membered rings **2a** or close 1,5 to form vinyl carbenes **2b**.[4,5] There are examples of each type of cyclization where X is either oxygen or carbon. When the initial product is **2b**, this intermediate stabilizes itself through some characteristic carbene reaction, with the particular products dependent upon structure and reaction conditions in each case. There is some evidence suggesting that 1,5 closure occurs specifically from triplet **1**,[5] and we believe that direct cyclization of triplet biradical to triplet carbene **2b** competes with the intersystem crossing that must accompany collapse of the biradical to a four-membered ring (**2a**). In several instances, formation of **2b** is the major or even sole pathway observed. With these findings in hand, we were interested in examining the photochemical cycloaddition of 3-alkynyl-2-cycloalken-1-ones with alkenes. Such reactions might offer a new route to alkyl propargyl 1,4-biradicals that could provide a novel type of [3 + 2] cycloaddition (eq 1). To the best of our knowledge, the only previously reported example of photocycloaddition in such a β-alkynyl α,β-unsaturated ketone involves simple solid state [2 + 2] dimerization of an open chain dienynone at one of the carbon–carbon double bonds.[6] There are also known photocycloadditions of alkenes with β-cyano α,β-unsaturated ketones and analogous 6-cyanouracils[7] that are at least formally akin to the reaction of eq 1, and these are discussed in more detail below, along with related intramolecular processes.[8] We have now explored such reactions with alkynylcycloalkenones and found that [3 + 2] addition does occur, furnishing in several instances a simple approach to complex systems. In this paper, we describe our examination of this process in the reactions of four substrates with four alkenes.[9]



(1)

† For our friend and colleague, Professor Kurt Schaffner, Max-Planck-Institut für Strahlenchemie, Mülheim a.d. Ruhr, on the occasion of his 60th birthday.

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(4) Hussain, S.; Agosta, W. C. *Tetrahedron Symposium-in-Print* **1981**, *37*, 3305. Rao, V. B.; Schröder, C.; Margaretha, P.; Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1985**, *50*, 3881. Margaretha, P.; Schröder, C.; Wolff, S.; Agosta, W. C. *J. Fluorine Chem.* **1986**, *30*, 429. Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 2363. Rao, V. B.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 521. Agosta, W. C.; Caldwell, R. A.; Jay, J.; Johnson, L. J.; Venepalli, B. R.; Scaiano, J. C.; Singh, M.; Wolff, S. *J. Am. Chem. Soc.* **1987**, *109*, 3050. Rudolph, A.; Margaretha, P.; Agosta, W. C. *Helv. Chim. Acta* **1987**, *70*, 339.
(5) Saba, S.; Wolff, S.; Schröder, C.; Margaretha, P.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 6902.
(6) Pochat, F.; Levas, E. *Bull. Soc. Chim. Fr.* **1972**, 4197.
(7) Saito, I.; Kanehira, K.; Shimozono, K.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 2737; Saito, I.; Shimozono, K.; Matsuura, T. *Ibid.* **1982**, *23*, 5439. Saito, I.; Shimozono, K.; Matsuura, T. *J. Am. Chem. Soc.* **1980**, *102*, 3948; Saito, I.; Shimozono, K.; Matsuura, T. *J. Org. Chem.* **1982**, *47*, 4356.
(8) Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1978**, *43*, 3627. Wolff, S.; Barany, F.; Agosta, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2378.
(9) Portions of this work have appeared in two preliminary communications: Margaretha, P.; Rathjen, H. J.; Wolff, S.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1988**, 841. Margaretha, P.; Rathjen, H.-J.; Agosta, W. C. *Tetrahedron Lett.* **1990**, *31*, 3245.

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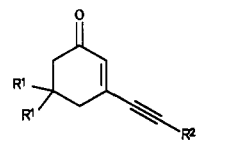
Table I. Distribution of Products from Cycloaddition of **3a,b,c** and **4** with **8–10**

entry	ketone	alkene	solvent	percent of isolated adducts[a] 1,4 closure	1,5 closure
1	**3a**	**8**	*t*-BuOH	total, 7% *t*-**14a**, 4%; *c*-**14a**, 3%	total, 93% **16a** + **17a**, 34%; **18a**, 50%; **19a**, 9%
2	**3b**	**8**	*t*-BuOH	total, <1%	total, >99% **16b** + **17b**, 29%; **19b**, 71%
3	**3c**	**8**	*t*-BuOH	total, 5% *t*-**14c**, 2%; *c*-**14c**, 3%	total, 95% **16c** + **17c**, 21%; **18c**, 55%; **19c**, 19%
4	**4**	**8**	CH_3CN	total, 17% **22**, 17%	total, 83% **20**, 44%; **21**, 39%
5	**4**	**8**	CH_3OH	total, 17% **22**, 17%	total, 83% **20**, 8%; **23**, 75%
6[b]	**4**	**8**	toluene or CH_3CN/toluene (9:1)	total, 87% **22**, 87%	total, 13% **20** + **21**, 13%
7[c]	**3a**	**9**	*t*-BuOH	total, 27% **26a** + **27a**, 27%	total, 50% **30a**, 36%; **31**, 6%; **32**, 8%
8[d]	**3c**	**9**	*t*-BuOH	total, 43% **26c**, 32%; **27c**, 11%	total, 43% **30c**, 43%
9	**3a**	**10**	benzene	total, 68% *t*-**39**, 52%; *c*-**39**, 16%	total, 32% **40**, 32%

[a] At ~40 °C, except entry 6. [b] At −60 °C. [c] Plus 23% oxetane **35a**. [d] Plus 14% oxetanes **35c** and **36c**.

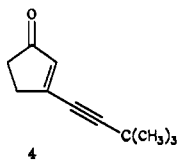
Preparative Reactions

Substrate ketones **3a**, **3c**, and **4** were available in 34–64% yield on addition of the Grignard reagent from 3,3-dimethyl-1-butyne to ethoxy enones **5**, **6**, and **7**, respectively, followed by acid hydrolysis.[10] Ketone **3b** was prepared similarly through addition of the Grignard reagent from propyne to **5**.



3

a, R^1 = H; R^2 = $C(CH_3)_3$
b, R^1 = H; R^2 = CH_3
c, R^1 = CH_3; R^2 = $C(CH_3)_3$



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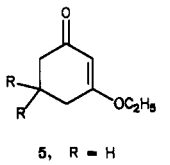
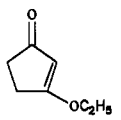


5, R = H
6, R = CH_3



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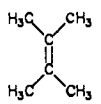

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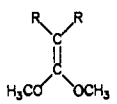
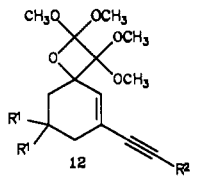


9, R = CH_3
10, R = H
11, R = OCH_3



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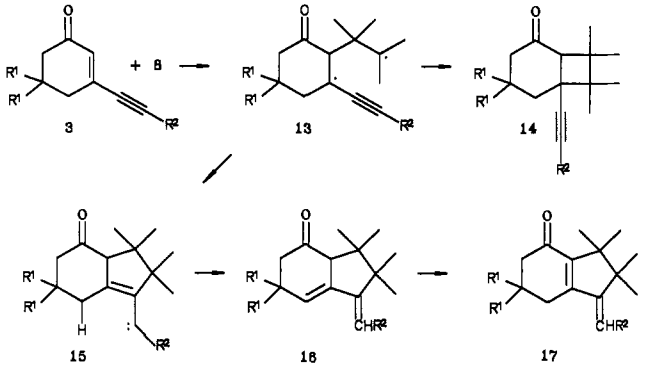
Results

Irradiation of each of these ynenones at λ ~350 nm with ~15 equiv of alkene led to mixtures of 1:1 adducts that typically included both 1,4 and 1,5 closure products. Control experiments established the stability of these products under the reaction conditions. Alkenes employed were tetramethylethylene (**8**), 1,1-dimethoxy-2-methylpropene (**9**),[11] 1,1-dimethoxyethylene (**10**),[12] and tetramethoxyethylene (**11**).[13,14] Preparative reactions were carried to ~95% conversion, and the total yields of volatile products were generally ~65%. Isolation and purification of individual products required multiple separations by gas chromatography or column chromatography over silica gel with considerable loss of material. Products were then identified by their spectroscopic properties. Our primary purpose has been to determine structural features and reaction conditions that permit 1,5 closure to compete successfully with normal [2 + 2] photocycloaddition, and Table I provides a summary of our results. This shows product distributions as determined by gas chromatographic examination of total reaction mixtures. For entries 7 and 8, the results were confirmed by ^1H NMR spectra of the reaction mixtures. Also tabulated is the overall distribution between 1,4 and 1,5 closure products in each case. Except for entry 6, results are for reactions at ~40 °C. As entry 6 shows, the product distribution in addition of **8** to **4** is temperature-dependent, with 1,4 addition strongly favored at −60 °C. The reactions between tetramethoxyethylene (**11**) and ketones **3a,c** are not included in Table I, since they produced oxetanes **12a,c** in high yield as the only isolated products. Lesser amounts of oxetanes were formed with **9** as the alkene (entries 7 and 8). These observations have precedent in the addition of **11** to simple cyclohexenones, where oxetanes are the major products.[15] As a rule, oxetane formation between simple enones and alkenes is uncommon,[15] and the anomalous behavior of **11** has been attributed to its unusually low ionization potential (6.82 eV).

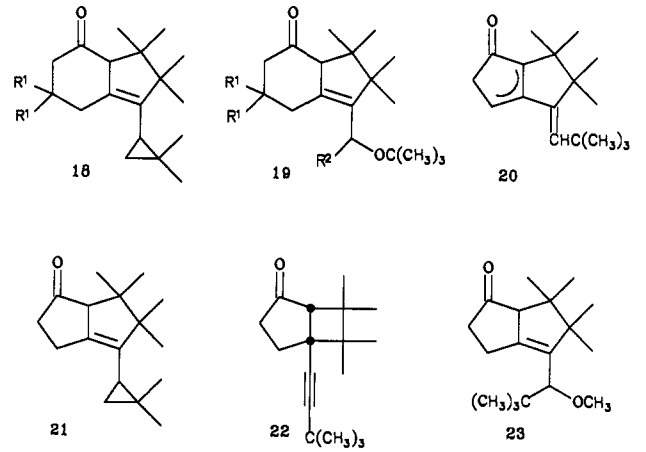
We turn now to the specific adducts formed in the reactions collected in Table I. Characterization of specific products is described in the Experimental Section, and in some cases this includes data on purified compounds listed as components of mixtures in Table I. For example, for both **16c** and **17c**, each of the possible geometric isomers was obtained pure and characterized and the stereochemical orientation about the double bond was assigned from comparison of ^1H NMR spectra. On the other hand, in some cases, mixtures of diastereomers, such as **21**, could not be separated by any method tried and characterization data are given for the mixture. In all cases, structures are in accord with spectroscopic properties (IR, UV, MS, and ^1H and ^{13}C NMR, as appropriate, along with elemental analysis or high-resolution MS of M^+) detailed in the characterization data.

Addition of tetramethylethylene (**8**) to the cyclohexenones **3a,b,c** (entries 1–3) presumably proceeds by way of biradical **13**.[16] In **3a** and **3c**, this intermediate undergoes a small amount of 1,4 closure to a mixture of cis- and trans-fused cyclobutanes **14**. No cyclobutanes were found with **3b**. The *trans*-**14** isomers underwent ready epimerization to *cis*-**14** on exposure to basic alumina at room temperature, and this isomerization provided the basis for assignment of their stereochemistry. Alternatively, **13** closes 1,5 to vinyl carbene **15**. Intramolecular hydrogen transfer in **15** gives the 3-cyclohexen-1-one **16** and, from this, the isomeric conjugated enone **17** on shift of the double bond. In **3a,c**, the major product from **15** is the cyclopropane **18**, which arises

(10) Spectroscopic data obtained for **3a** were in agreement with those previously reported for this ketone prepared by another route: Schwartz, J.; Hayasi, Y. *Tetrahedron Lett.* **1980**, *21*, 1497.
(11) McElvain, S. M.; Davie, W. R. *J. Am. Chem. Soc.* **1951**, *73*, 1400.
(12) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.
(13) Bellus, D.; Fischer, H.; Greuter, H.; Martin, P. *Helv. Chim. Acta* **1978**, *61*, 1784.
(14) Reaction of mono- and disubstituted alkenes such as cyclopentene, isobutylene, trimethylvinylsilane, and ethyl vinyl ether with these ketones yielded no [3 + 2] adducts under our reaction conditions. *trans*-Fused cyclobutanes were formed preferentially from **3a,b,c** and the acyclic alkenes of this group: Rathjen, H.-J. Ph.D. Dissertation, Universität Hamburg, 1991.
(15) Cruciani, G.; Rathjen, H.-J.; Margaretha, P. *Helv. Chim. Acta* **1990**, *73*, 856.

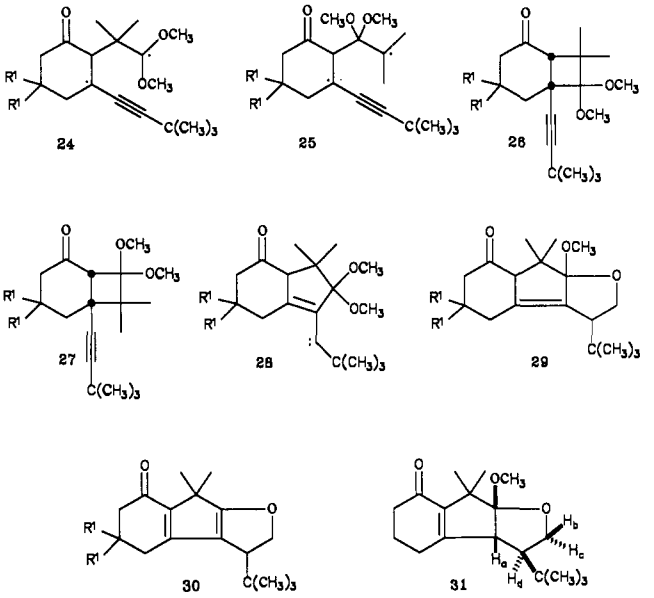


through carbene insertion into a methyl hydrogen of the *tert*-butyl group. With *tert*-butyl alcohol as solvent, insertion of **15** into

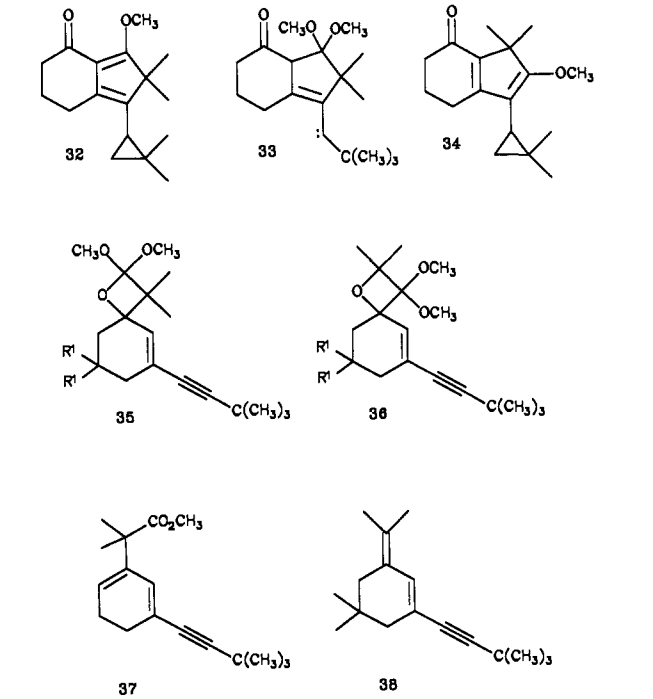


solvent occurs to a smaller extent to furnish **19**. All of these reactions of **15** are known carbene processes that also have precedent in earlier studies of alkyl propargyl biradicals.[4,5] Addition of **8** to the cyclopentenone **4** in acetonitrile and in methanol gives comparable distribution between 1,4 and 1,5 products (entries 4 and 5). The distribution is also similar in acetonitrile/toluene (9:1), toluene, benzene, dichloromethane, and *tert*-butyl alcohol as solvents (data not shown). Both hydrogen transfer products **20** and cyclopropane **21** were found, along with [2 + 2] adduct **22**. In methanol, the carbene yields largely solvent adduct **23**, but in *tert*-butyl alcohol (data not shown) no such alcohol adduct is found.

Addition of **9** to **3a,c** (entries 7 and 8) proceeds primarily by way of biradical **24**[16] to give [2 + 2] product **26** and carbene **28**, plus a minor amount of reaction through the isomeric biradical **25**, which is the precursor of **27**. Cyclobutanes **26** and **27** do not undergo epimerization in the presence of alumina and are accordingly assigned the cis stereochemistry shown. The regiochemistry of geminal methyl and methoxy substituents on the cyclobutane rings in **26** and **27** follows from the greater chemical shift in **27** (δ ~3.1 ppm) than in **26** (δ ~2.4 ppm) of the unique bridgehead proton.[17] In **28**, the methoxy groups provide an added pathway for reaction of the carbene. Insertion into a methoxy



C–H bond leads initially to **29**, which largely undergoes elimination of methanol to form **30**. In this odd overall sequence of reactions, both methoxy groups of **9** have disappeared, one incorporated into a five-membered ring and the other eliminated as methanol. Along with **30a**, there is obtained from **3a** a small amount of **31**, where the double bond of **29a** has simply moved into conjugation without vinylogous loss of methanol. The stereochemistry of the ring junction formed on prototropic shift can be assigned cis in view of the relative stability of cis-fused bicyclo[3.3.0]octanes, and the orientation of the *tert*-butyl group in **31** is tentatively assigned from comparison of the vicinal coupling constants J_{ad}, J_{bd}, and J_{cd} with values predicted from molecular mechanics calculations.[18] In addition, this cycloaddition with **3a** also produces a small amount of **32**, formed from 1,5 closure of **25** to carbene **33**.



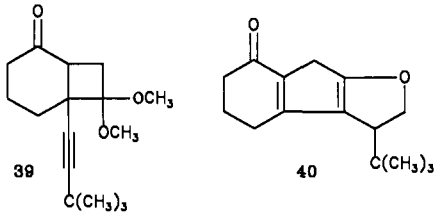
(16) Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123. Weedon, A. C. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1984; pp 61–143. Schuster, D. I. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; p 623. Cruciani, G.; Semisch, C.; Margaretha, P. *J. Photochem. Photobiol., A* **1988**, *44*, 219. Rudolph, A.; Weedon, A. C. *Can. J. Chem.* **1990**, *68*, 1590.

(17) According to molecular mechanics calculations, in the lowest energy conformations of **26a** and **27a**, the distance from the bridgehead methine hydrogen to the nearer methoxy oxygen is 3.00 and 2.46 Å, respectively. This should assure that the field effect of methoxy on this proton chemical shift is greater in **27a**, as expected. These and later described molecular mechanics calculations made use of MMX, an adaptation by J. J. Gajewski and K. E. Gilbert (*cf.* Midland, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 5042) of MM2 (Allinger, N. L.; Yuh, Y. H. *QCPE* **1981**, *13*, 395) with π-subroutines from MMI/MMPI (Allinger, N. L.; et al. *QCPE* **1976**, *11*, 318) and PCMODEL, both as distributed by Serena Software, Bloomington, IN.

(18) The $\Delta\Delta H_f$ for *cis*- and *trans*-bicyclo[3.3.0]octane as determined by calorimetry is 6.0 kcal/mol: Barrett, J. W.; Linstead, R. P. *J. Chem. Soc.* **1935**, 436. Roberts, J. D.; Gorham, W. F. *J. Am. Chem. Soc.* **1952**, *74*, 2278. Granger, R.; Nau, P. F. G.; Nau, J. *Bull. Soc. Chim. Fr.* **1960**, 1225. Molecular mechanics calculations suggest that J_{ad}, J_{bd}, and J_{cd} should be, respectively, 5.5, 11.0, and 7.9 Hz for **31** and 10.4, 0.9, and 4.9 Hz for the epimer of **31** with opposite stereochemistry of the *tert*-butyl group. Observed values are 4.3 Hz for J_{ad} and 8.6 and 9.0 Hz for J_{bd} and J_{cd}.

Carbene insertion into the *tert*-butyl group of **33** and elimination of methanol lead to **32**. We note that these same steps, starting from carbene **28** rather than **33**, would furnish the isomeric product **34**. We tentatively formulate this minor product as **32**, however, on the basis of its ultraviolet spectrum, λ_{max} 319 nm (log ϵ 3.85). The λ_{max} of **34** should be at longer wavelength, resembling the spectra of **30a,c**, which have λ_{max} 344–345 nm (log ϵ ~3.67). Finally, ^{1}H NMR spectra of the crude product mixtures from **3a,c** and **9** suggested the presence of minor amounts of oxetanes **35a,c** and **36c**. Adducts **35** decomposed on attempted isolation, but **37** and **38** could be isolated from fragmentation of **35a** and **35c**, respectively. These two dienynes were purified and characterized. Adduct **36c** was characterized, and the regiochemistry of substituents on the oxetane ring was assigned from examination of its mass spectrum. This has a prominent fragment at $(M - 58)^+$, corresponding to loss of the elements of acetone through fragmentation of the four-membered ring.

Reaction of **3a** with 1,1-dimethoxyethylene (**10**) (entry 9) gives less [3 + 2] addition, the main products being the cis and trans [2 + 2] adducts **39** accompanied by **40**, the tricyclic product corresponding to **30**.

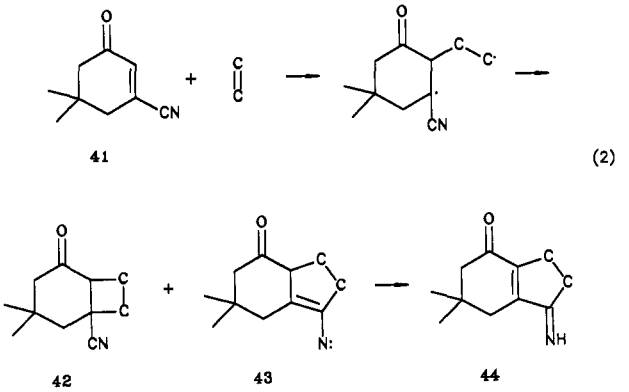


Discussion

The results compiled in Table I indicate that [3 + 2] cycloaddition in these alkynylcycloalkenones is relatively insensitive to distant substitution in the ketone (cf. behavior of **3a** and **3c**), to steric bulk of the alkyl substituent on the triple bond (cf. behavior of **3a** and **3b**), and to solvent polarity. The mode of cycloaddition is quite sensitive, however, to the nature of the alkene, with **8** and **9** yielding more [3 + 2] addition than **10** and the omitted simple monosubstituted ethylenes giving none at all.[14] Since addition of **10** furnishes some carbene-derived product and reaction with isobutylene does not,[14] this sensitivity to alkene structure may be more than a simple steric effect. In this regard, it is worth noting that there is a simple correlation between the course of these cycloadditions and the ionization potential (IP) of the adding alkene: Isobutylene and ethyl vinyl ether, IP > 9 eV, yield only cyclobutanes and disproportionation products;[14] **8–10**, IP ~8–8.5 eV, yield mainly [3 + 2] adducts; and **11**, IP < 7 eV, yields only oxetanes.[19] The only previously described processes known to us that appear to be closely related to these [3 + 2] cycloadditions are the photochemical reactions of certain alkenes with **41** and related cyano-substituted unsaturated systems, which in general lead to both **42** and **44** (eq 2).[7] It is noteworthy that the course of this reaction also displays an important dependence on alkene structure. For example, cyclohexene adds only [2 + 2] to **41**, while 1-methylcyclohexene gives both [2 + 2] and [3 + 2] products.

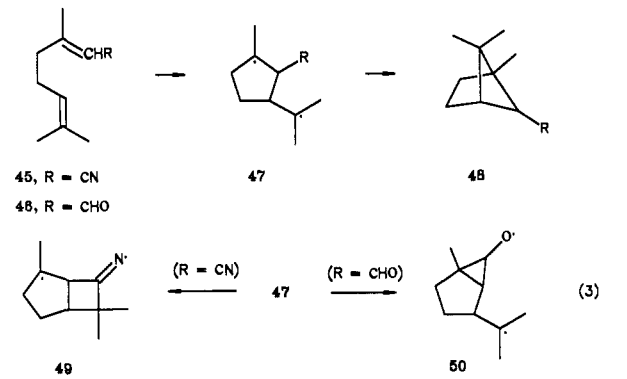
Formation of appreciable amounts of trans-fused cyclobutanes from **3a,b,c** indicates that much of the 1,4 closure, and perhaps also 1,5 closure, takes place from twisted, unrelaxed conformations of the biradical.[16] The factors controlling the partitioning of unrelaxed biradicals between 1,4 and 1,5 closure must be complex. They will include those factors that influence normal [2 + 2] cycloaddition, which have been under vigorous discussion for over 25 years,[16] as well as other, as yet unidentified, factors concerned specifically with 1,5 cyclization.

We were also interested in the possible effect of temperature on 1,4 and 1,5 closure. It was attractive to examine this question



with use of addition of **8** to **4**, since this reaction leads to fewer products than the other cycloadditions studied and, therefore, simpler analysis by gas chromatography. Entry 6 reveals that, at −60 °C, 1,4 closure has become the dominant process. We note that this large temperature effect is consistent with our earlier suggestion that closure of alkyl propargyl biradicals to vinyl carbenes occurs from the triplet biradical without prior intersystem crossing.[5] The rate-controlling step in normal reactions of triplet biradicals, including coupling, is intersystem crossing to the singlet, the rate of which shows very little dependence upon temperature.[20] Under these circumstances, if the rate-controlling step(s) leading to products derived from 1,5 closure require activation, these products should become relatively more favorable with increasing temperature. While nothing is yet known about the kinetics of 1,5 closure and the subsequent transformations of the vinyl carbene, it is reasonable to assume that these steps require activation.[21]

There is a similar temperature dependence in alkene addition to **41**, where the relative amount of [3 + 2] adduct also increases with temperature.[7] Moreover, a parallel effect exists in the intramolecular photochemistry of geranonitrile (**45**), citral (**46**), and related compounds.[8] For example, at room temperature, biradical **47** undergoes ordinary disproportionation and closure to the [2 + 2] products **48**;[8,22] competitive closure to **49** and **50** (eq 3) and



formation of photoproducts derivable from these isomeric biradicals take place only at elevated temperature.[23] We note that, in all these systems, the proportion of normal 1,4 closure decreases with temperature and that this behavior is consistent with the hypothesis that formation of **43**, **49**, and **50** also involves direct

(19) Ionization potentials are taken or estimated from Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213. Bloch, M.; Brogli, E.; Heilbronner, E.; Jones, T. B.; Prinzbach, H.; Schwenkert, O. *Ibid.* **1978**, *61*, 1388.

(20) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521. Caldwell, R. A. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; Chapter 4, p 77.

(21) Data presently at hand do not distinguish between (1) reversible closing of triplet biradical to triplet carbene, with rate-controlling steps following in conversion of carbene to final products, and (2) irreversible, rate-controlling closure of biradical to carbene. In either case, it is expected that $\Delta H^{\ddagger} > 0$ for the rate-controlling step(s).

(22) Cookson, R. C.; Hudec, J.; Knight, S. A.; Whitear, B. R. D. *Tetrahedron* **1963**, *19*, 1995. Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1965**, *87*, 1589.

(23) Possible alternatives to **50** as an intermediate are discussed in the original paper.

cyclization of triplet biradicals in competition with intersystem crossing to the singlet. Owing to the insensitivity to temperature of the rate of intersystem crossing, triplet–triplet rearrangements of biradicals should be favored in general by increasing temperature. In contrast, the temperature dependence of the cis/trans ratio of products in ordinary [2 + 2] photocycloadditions appears simply to reflect the $\Delta\Delta F^{\ddagger}$ for two modes of closure of a common biradical intermediate.[24]

Mechanistic problems obviously still remain in understanding these multistep processes. Nonetheless, it is worth noting at this early stage that the [3 + 2] cycloaddition reactions reported here provide easy, single-step access to relatively complex systems such as **18**, **23**, and **30**.

Experimental Section

General Information. NMR spectra are reported for $CDCl_3$ solutions at 400 MHz for ^1H and 100.63 MHz for ^{13}C. Mass spectra are at 70 eV. Analytical gas chromatography was carried out on a Carlo Erba Fractovap 2150 instrument fitted with a 25-m glass capillary SE-30 column and a Hewlett-Packard 3390 integrator. Preparative gas chromatography employed a Shimadzu GC-8a instrument fitted with a 4 m × 8 mm steel column packed with 5% SE-30 on Chromosorb W-AW-DCMS, 80/100 mesh. Irradiations were carried out in a Rayonet RPR-100 Photoreactor equipped with 16 350-nm lamps. All purified products were obtained as colorless oils unless otherwise indicated.

Preparation of 3-Alkynyl-2-cycloalken-1-ones 3a–c and 4. Details are given for **3a**. Under N_2 at room temperature, 3.73 g (28 mmol) of C_2H_5MgBr in 20 mL of absolute THF was treated dropwise with 2.5 g (30 mmol) of 3,3-dimethyl-1-butyne, and the resulting mixture was heated at reflux for 1 h. The solution was cooled, and at room temperature 3.5 g (25 mmol) of **5** in 5 mL of THF was added dropwise. After 30 min of heating at reflux, the cooled solution was poured into cold saturated aqueous NH_4Cl and extracted three times with ether. After usual washing, drying, and removal of ether, the residue was dissolved in 40 mL of methanol and stirred for 2 h at room temperature with 4 mL of saturated aqueous oxalic acid solution. Most of the methanol was distilled off, and the organic residue was worked up in the usual way with pentane. The residue from removal of pentane was distilled; bp 68–73 °C (0.05 Torr), mp 31–32 °C (64%). Data for **3a**: IR (KBr) 2950 (m), 2200 (w), 1660 (vs) cm^{-1}; ^1H NMR δ 6.3 (t, J = 1 Hz, 1 H), 2.5–2.3 (m, 4 H), 2.1–1.9 (m, 2 H), 1.29 (s, 9 H); ^{13}C NMR δ 197.5, 143.6, 131.2, 109.0, 78.5, 36.7, 30.4 (3×), 30.1, 27.8, 22.1; UV (C_6H_{12}) λ_{max} 345 nm (ϵ 40.2); MS m/z 176 (M^+, 69), 105 (100); HRMS m/z 176.0076 (M^+, calcd for $C_{12}H_{16}O$ 176.0074).[10]

The same procedure was used with the appropriate cycloalkenone for **3b,c** and **4**, except that, for **3b**, a saturated solution of propyne was employed; for **3b** and **4**, workup made use of CH_2Cl_2 rather than pentane, and for **3c** final purification was by column chromatography over silica gel, in 9:1 petroleum ether/ethyl acetate.

Data for **3b**: bp 44 °C (0.1 Torr) (41%); IR (KBr) 2950 (m), 2200 (w), 1660 (vs) cm^{-1}; ^1H NMR δ 6.13 (s, 1 H), 2.46–2.34 (m, 4 H), 2.07 (s, 3 H), 2.05–1.97 (m, 2 H); ^{13}C NMR δ 198.1, 144.0, 131.4, 97.3, 79.2, 36.9, 30.4, 22.2, 4.3; UV (C_6H_{12}) λ_{max} 351 nm (ϵ 42.7); MS m/z 134 (M^+, 86), 106 (100); HRMS m/z 134.0041 (M^+, calcd for $C_9H_{10}O$ 134.0027).

Data for **3c**: mp 37–38 °C (34%) IR (KBr) 2950 (m), 2200 (w), 1660 (vs) cm^{-1}; ^1H NMR δ 6.13 (t, J = 1.8 Hz, 1 H), 2.31 (d, J = 1.8 Hz, 2 H), 2.23 (s, 2 H), 1.28 (s, 9 H), 1.05 (s, 6); ^{13}C NMR δ 197.7, 141.4, 130.4, 108.8, 78.9, 50.8, 44.7, 33.2, 30.4 (3×), 28.0, 27.8 (2×); UV (C_6H_{12}) λ_{max} 353 nm (ϵ 40.4); MS m/z 204 (M^+, 60), 105 (100); HRMS m/z 204.0110 (M^+, calcd for $C_{14}H_{20}O$ 204.0105).

Data for **4**: bp 41–42 °C (0.02 Torr); mp 24 °C (62%); IR (CCl_4) 2973 (m), 2184 (w), 1714 (vs) cm^{-1}; ^1H NMR δ 6.2 (t, J = 1.8 Hz, 1 H), 2.73–2.64 (m, 2 H), 2.45–2.35 (m, 2 H), 1.3 (s, 9 H); ^{13}C NMR δ 209.1, 158.0, 135.3, 115.0, 75.7, 34.8, 32.9, 30.6 (3×), 28.6; UV (C_6H_{12}) λ_{max} 342 nm (ϵ 35.9); MS m/z 162 (M^+, 40), 91 (100); HRMS m/z 162.0063 (M^+, calcd for $C_{11}H_{14}O$ 162.0058).

Photochemical Procedures. A mixture of 3.5 mmol of the appropriate ketone and 52.5 mmol of alkene in 29 mL of solvent was flushed for 20 min with argon and then irradiated to ~95% conversion (2.5–16 h) at λ ~350 and ~40 °C. Solvent was distilled off under vacuum, and the residue was worked up by successive chromatographic separations. Distribution of products was determined by analytical gas chromatography before separation, and results are given in Table I. trans-Fused cyclobutanes *trans*-**14a,c** and *trans*-**39** were completely epimerized to the corresponding cis isomers on exposure to basic alumina at room temperature. *trans*-**14a,c** could not be obtained pure for characterization. Characterization data are given below, by entry in Table I.

Entry 1. Irradiation for 5 h. Data for *cis*-**14a**: ^1H NMR δ 2.74 (s, 1 H), 2.58–1.7 (m, 6 H), 1.21 (s, 3 H), 1.19 (s, 9 H), 1.16 (s, 3 H), 1.15 (s, 3 H), 0.96 (s, 3 H); MS m/z 260 (M^+, 3), 177 (100); HRMS m/z 260.0173 (M^+ calcd for $C_{18}H_{28}O$ 260.0168). Data for **16a**: ^1H NMR δ 6.18 (m, 1 H), 5.2 (s, 1 H), 2.81 (s, 1 H), 2.76–2.4 (m, 4 H), 1.21 (s, 9 H), 0.98 (s, 3 H), 0.92 (s, 3 H), 0.90 (s, 3 H), 0.88 (s, 3 H); MS m/z 260 (M^+, 60), 189 (100); HRMS m/z 260.0172 (M^+, calcd for $C_{18}H_{28}O$ 260.0168). Data for **17a**: ^1H NMR δ 5.66 (s, 1 H), 2.70–1.90 (m, 6 H), 1.21 (s, 9 H), 1.09 (s, 6 H), 0.94 (s, 6 H); MS m/z 260 (M^+, 40), 189 (100); HRMS m/z 260.0173 (M^+, calcd for $C_{18}H_{28}O$ 260.0168). Data for **18a** (mixture of two diasteromers): ^1H NMR δ 3.04 and 2.95 (m, ~1 H each), 1.2, 1.15 (2×), 1.1, 0.95, 0.90, 0.87, 0.86, 0.84, 0.83, 0.80, 0.78 (s each ~3 H), 0.7–0.6 (m, 2 H); ^1H NMR (C_6D_6) (a) δ 2.88 (m, 1 H), 0.73 (dd, J = 4.2, 6.4 Hz, 1 H), 0.54 (dd, J = 4.2, 8.7 Hz, 1 H) and (b) δ 2.72 (m, 1 H), 0.66 (dd, J = 4.4, 6.3 Hz, 1 H), 0.49 (dd, J = 4.4, 9.0, 1 H); gated ^{13}C NMR (C_6D_6) (a) δ 19.0 (J = 159 Hz) and (b) δ 18.1 (J = 159 Hz); MS m/z 260 (M^+, 60), 189 (100); HRMS m/z 260.0175 (M^+, calcd for $C_{18}H_{28}O$ 260.0168). Data for **19a** (mixture of two diastereomers): ^1H NMR (a) δ 3.69 (s, 1 H), 2.84 (s, 1 H), 1.19 (s, 9 H), 0.95 (s, 9 H) and (b) δ 4.26 (s, 1 H), 3.05 (s, 1 H), 1.18 (s, 9 H), 0.95 (s, 9 H); MS (CI) m/z 335 ($(M + 1)^+$, 10), 261 (100). Anal. ($C_{22}H_{38}O_2$) C, H.

Entry 2. Irradiation for 16 h. Data for **16b**: ^1H NMR δ 6.25 (m, 1 H), 5.51 (q, J = 7.6 Hz, 1 H), 2.9 (s, 1 H), 2.6–2.1 (m, 4 H), 1.88 (d, J = 6.7, 3 H), 1.15 (s, 3 H), 0.93 (s, 3 H), 0.89 (s, 3 H), 0.68 (s, 3 H); MS m/z 218 (M^+, 91), 203 (100). Data for **17b**: 5.55 (q, J = 7.6 Hz, 1 H), 2.7–2.1 (m, 6 H), 1.91 (d, J = 7.6 Hz, 3 H), 1.05 (s, 6 H), 0.91 (s, 6 H); MS m/z 218 (M^+, 91), 203 (100). Data for **19b** (mixture of two diastereomers): ^1H NMR (a) δ 4.45 (q, J = 6.6 Hz, 1 H), 2.97 (s, 1 H), 2.14–1.6 (m, 6 H), 1.26 (d, J = 6.6 Hz, 3 H), 1.19 (s, 9 H), 1.15–0.8 (4 s, 12 H) and (b) δ 4.2 (q, J = 6.6 Hz, 1 H), 2.91 (s, 1 H), 2.4–1.6 (m, 6 H), 1.25 (d, J = 6.6 Hz, 2 H), 1.19 (s, 9 H), 1.15–0.8 (4 s, 12 H); MS m/z 292 (M^+, 2), 203 (100); HRMS m/z 292.0155 (M^+, calcd for $C_{19}H_{32}O_2$ 292.0148).

Entry 3. Irradiation for 7 h. Data for *cis*-**14c**: ^1H NMR δ 2.76 (s, 1 H), 2.21 (d, J = 13.8 Hz, 1 H), 2.10 (d, J = 13.8 Hz, 1 H), 2.02 (d, J = 16.7 Hz, 1 H), 1.67 (d, J = 16.7 Hz, 1 H), 1.20 (s, 3 H), 1.14 (s, 9 H), 1.07 (s, 3 H), 1.06 (s, 3 H), 1.04 (s, 3 H), 1.02 (s, 3 H), 0.97 (s, 3 H); MS m/z 288 (M^+, 0.2), 205 (100). Anal. ($C_{20}H_{32}O$) C, H. Data for (*E*)-**16c**: ^1H NMR δ 6.07 (d, J = 2.8 Hz, 1 H), 5.34 (s, 1 H), 2.84 (d, J = 2.8 Hz, 1 H), 2.34 (d, J = 14.4 Hz, 1 H), 2.11 (d, J = 14.4 H z, 1 H), 1.20 (s, 9 H), 1.15 (s, 3 H), 1.11 (s, 3 H), 1.09 (s, 3 H), 0.91 (s, 3 H), 0.90 (s, 3 H), 0.69 (s, 3 H); MS m/z 288 (M^+, 36), 273 (100); HRMS m/z 288.0204 (M^+, calcd for $C_{20}H_{32}O$ 288.0199). Data for (*Z*)-**16c**: ^1H NMR δ 6.0 (s, 1 H), 5.2 (s, 1 H), 2.74 (s, 1 H), 2.44 (d, J = 12.6 Hz, 1 H), 2.3 (d, J = 12.6 Hz, 1 H), 1.22 (s, 9 H), 1.03 (s, 3 H), 1.0 (s, 3 H), 0.97 (s, 3 H), 0.92 (s, 3 H), 0.90 (s, 3 H), 0.84 (s, 3 H); MS m/z 288 (M^+, 6), 57 (100); HRMS m/z 288.0201 (M^+ calcd for $C_{20}H_{32}O$ 288.0199). Data for (*E*)-**17c**: ^1H NMR δ 5.73 (s, 1 H), 2.24 (s, 2 H), 2.17 (s, 2 H), 1.26 (s, 9 H), 1.15 (s, 6 H), 1.05 (s, 6 H), 1.04 (s, 6 H); ^{13}C NMR δ 198.0, 158.3, 151.7, 142.3, 139.3, 53.1, 48.9, 48.7, 37.7, 33.9, 32.7, 32.4, 28.6, 24.3, 22.1; MS m/z 288 (M^+, 58), 217 (100); HRMS m/z 288.0201 (M^+, calcd for $C_{20}H_{32}O$ 288.0199). Data for (*Z*)-**17c**: IR (film) 2961 (s), 1650 (vs), 1578 (m), 1468 (m), 1404 (vs) cm^{-1}; ^1H NMR δ 5.5 (s, 1 H), 2.6 (s, 2 H), 2.25 (s, 2 H), 1.21 (s, 9 H), 1.08 (s, 6 H), 1.04 (s, 6 H), 0.91 (s, 6 H); ^{13}C NMR δ 198.1, 153.6, 150.4, 146.8, 139.3, 52.8, 51.5, 46.6, 43.1, 34.9, 32.5, 32.2, 28.3, 24.7, 21.8; MS m/z 288 (M^+, 40), 245 (100); HRMS m/z 288.0205 (M^+, calcd for $C_{20}H_{32}O$ 288.0199). Data for **18c** (mixture of two diastereomers): IR (film) 2960 (vs), 1709 (s), 1679 (s), 1466 (m), 1368 (s) cm^{-1}; ^1H NMR (bridgehead methine and cyclopropane methylene protons only) (a) δ 2.88 (m, 1 H), 0.71 (dd, J = 6.5, 4.4 Hz, 1 H), 0.62 (dd, J = 8.8, 4.4 Hz, 1 H) and (b) δ 2.86 (m, 1 H), 0.63 (dd, J = 8.8, 4.4, 1 H); ^{13}C NMR (omitting quaternary and methyl carbons) (a) δ 209.4, 141.4, 131.5, 63.4, 55.6, 39.5, 30.7, 18.5 and (b) δ 208.0, 140.7, 132.0, 63.2, 55.4, 39.7, 31.0, 19.1; MS m/z 288 (M^+, 91), 273 (100); HRMS m/z 288.0203 (M^+, calcd for $C_{20}H_{32}O$ 288.0199). Data for **19c** (mixture of two diasteromers): ^1H NMR (partial spectra only) (a) δ 3.69 (s, 1 H), 2.75 (s, 1 H), 1.18 (s, 9 H), 0.96 (s, 9 H) and (b) δ 4.25 (s, 1 H), 2.95 (s, 1 H), 1.17 (s, 9 H), 0.98 (s, 9 H); MS (CI) m/z 363 ($(M + 1)^+$, 17), 289 (100). Anal. ($C_{24}H_{42}O_2$) C, H.

Entry 4. Irradiation for 4 h. Data for **20** (β,γ-double bond): H^1 NMR δ 6.03 (ddd, J = 2.2, 2.4, 2.6, 1 H), 5.26 (s, 1 H), 3.05 (ddd, J = 24.0, 2.4, 1.0 Hz, 1 H), 2.91 (dd, J = 2.2, 1.0 Hz, 1 H), 2.90 (dd, J = 24.0, 2.6 Hz, 1 H), 1.22 (s, 9 H), 1.20 (s, 3 H), 0.96 (s, 3 H), 0.92 (s, 3 H), 0.70 (s, 3 H); MS m/z 246 (M^+, 76), 57 (100); HRMS m/z 246.0153 (M^+, calcd for $C_{17}H_{26}O$ 246.0152). Data for **20** (α,β-double bond): ^1H NMR δ 5.71 (s, 1 H), 2.80 (m, 2 H), 2.42 (m, 2 H), I.20 (s,

(24) See, for example: Margaretha, P. *Liebigs Ann. Chem.* **1973**, 727.

9 H), 1.12 (s, 6 H), 0.92 (s, 6 H); ^{13}C NMR δ 207.3, 165.3, 144.0, 141.1, 140.5, 39.1, 36.8, 35.7, 34.4, 30.0 (3×), 27.9, 22.0 (2×), 19.3 (2×); MS m/z 246 (M^+, 53), 175 (100); HRMS m/z 246.0160 (M^+, calcd for $C_{17}H_{26}O$ 246.0152). Data for **21** (mixture of two diastereomers): ^{1}H NMR (partial spectra) bridgehead proton (a) δ 2.71 (dd, J = 2.4, 2.4 Hz, 1 H) and (b) δ 2.62 (s, 1 H), cyclopropane methylene (a) δ 0.65 (dd, J = 6.0, 4.3 Hz, 1 H), 0.49 (dd, J = 8.7, 4.3 Hz, 1 H), and (b) δ 0.68 (dd, J = 6.2, 4.2 Hz, 1 H), 0.55 (dd, J = 8.4, 4.2 Hz, 1 H); ^{13}C NMR (partial spectra) (a) δ 139.7, 135.1, 65.2 and (b) δ 140.1, 134.9, 64.6; MS m/z 246 (M^+, 25), 175 (100); HRMS m/z 246.0163 (M^+, calcd for $C_{17}H_{26}O$ 246.0152). Data for **22**: ^{1}H NMR δ 2.60–2.33 (m, 3 H), 2.41 (s, 1 H), 2.10–2.00 (m, 1 H), 1.21 (s, 9 H), 1.19 (s, 3 H), 1.18 (s, 3 H), 1.00 (s, 3 H), 0.92 (s, 3 H); ^{13}C NMR (C_6D_6) δ 91.9, 83.6, 60.9, 43.1, 42.7, 41.4, 40.2, 31.4, 30.6, 27.6, 27.4, 24.8, 21.5, 20.8; MS (CI) 247 ((M + 1)$^+$, 44), 163 (100). Anal. ($C_{17}H_{26}O$) C, H.

Entry 5. Irradiation for 6 h. Data for **23** (mixture of two diastereomers): ^{1}H NMR (a) δ 3.35 (s, 1 H), 3.31 (s, 3 H), 2.56–2.23 (m, 4 H), 1.11 (s, 3 H), 1.02 (s, 3 H), 0.95 (s, 9 H), 092 (s, 3 H), 0.88 (s, 3 H) and (b) δ 3.29 (s, 1 H), 3.21 (s, 3 H), 2.60–2.20 (m, 4 H), 1.11 (s, 3 H), 1.01 (s, 3 H), 1.00 (s, 9 H), 0.91 (s, 3 H), 0.87 (s, 3 H); MS (CI) 279 ((M + 1)$^+$, 3), 247 (100). Anal. ($C_{18}H_{30}O_2$) C, H.

Entry 6. Conversion ~50%.

Entry 7. Irradiation for 4.5 h. Data for **26a**: ^{1}H NMR δ 3.47 (s, 3 H), 3.27 (s, 3 H), 2.48–1.80 (m, 6 H), 2.44 (s, 1 H), 1.28 (s, 3 H), 1.19 (s, 9 H), 1.11 (s, 3 H); MS m/z 292 (M^+, 4), 116 (100); HRMS m/z 292.2041 (M^+, calcd for $C_{18}H_{28}O_3$ 292.2038). Data for **27a**: ^{1}H NMR δ 3.27 (s, 3 H), 3.20 (s, 3 H), 3.06 (s, 1 H), 2.5–2.14 (m, 3 H), 1.96–1.68 (m, 3 H), 1.20 (s, 3 H), 1.17 (s, 9 H), 1.12 (s, 3 H); ^{13}C NMR δ 209.6, 105.8, 91.9, 81.1, 59.2, 51.0, 50.6, 50.4, 41.1, 38.3, 31.4, 30.0, 27.4, 23.9, 21.1, 18.3; MS m/z 292 (M^+, 2), 116 (100); HRMS m/z 292.2039 (M^+, calcd for $C_{18}H_{28}O_3$ 292.2038). Data for **30a**: IR (film) 1695, 1677, 1630, 1615 cm^{-1}; ^{1}H NMR δ 4.85 (dd, J = 4.5, 9.8 Hz, 1 H), 4.78 (dd, J = 8.7, 9.8 Hz, 1 H), 2.88 (dd, J = 4.5, 8.7 Hz, 1 H), 2.63–2.53 (m, 2 H), 2.39–2.32 (m, 2 H), 2.14–1.85 (m, 2 H), 1.34 (s, 3 H), 1.3 (s, 3 H), 0.91 (s, 9 H); ^{13}C NMR δ 191.4, 189.2, 161.0, 138.5, 118.3, 82.6, 50.6, 42.7, 37.8, 33.7, 27.1 (3×), 26.9, 24.0, 20.91, 20.87; UV (C_6H_{12}) λ_{max} 344 nm (log ϵ 3.71); MS m/z 260 (M^+, 18), 203 (100); HRMS m/z 260.1782 (M^+, calcd for $C_{17}H_{24}O_2$ 260.1776). Data for **31**: ^{1}H NMR δ 4.0 (dd, J = 8.6, 8.6 Hz, 1 H), 3.66 (dd, J = 9.0, 9.0 Hz, 1 H), 3.32 (s, 3 H), 2.91 (d, J = 4.3 Hz, 1 H), 2.44–1.91 (m, 7 H), 1.44 (s, 3 H), 1.21 (s, 3 H), 0.94 (s, 9 H); MS m/z 292 (M^+, 11), 234 (100); HRMS m/z 292.2042 (M^+, calcd for $C_{18}H_{28}O_3$ 292.2038). Data for **32**: ^{1}H NMR δ 4.03 (s, 3 H), 2.55–2.31 (m, 4 H), 2.15–1.91 (m, 2 H), 1.3 (dd, J = 6.0, 8.6 Hz, 1 H), 1.21 (s, 6 H), 1.18 (s, 3 H), 0.90 (s, 3 H), 0.8 (dd, J = 4.2, 8.6 Hz, 1 H), 0.55 (dd, J = 4.2, 6.0 Hz, 1 H); UV (C_6H_{12}) λ_{max} 319 nm (log ϵ 3.85); MS m/z 260 (M^+, 100); HRMS m/z 260.1778 (M^+, calcd for $C_{17}H_{24}O_2$ 260.1776). Data for **37a** (formed on attempted purification of **35a**): ^{1}H NMR δ 6.1 (s, 1 H), 5.68 (m, 1 H), 3.66 (s, 3 H), 2.20 (m, 4 H), 1.31 (s, 6 H), 1.26 (s, 9 H); ^{1}H NMR (C_6D_6) δ 6.56 (dd, J = 1.3, 1.4 Hz, 1 H), 5.54 (dt, J = 1.4, 4.7 Hz, 1 H), 3.25 (s, 3 H), 2.24 (dt, J = 1.3, 9.6 Hz, 2 H), 1.97 (dt, J = 4.7, 9.6 Hz, 2 H), 1.30 (s, 6 H), 1.21 (s, 9 H); MS m/z 260 (M^+, 60), 159 (100); HRMS m/z 260.1782 (M^+, calcd for $C_{17}H_{24}O_2$ 260.1776).

Entry 8. Irradiation for 5 h. Data for **26c**: ^{1}H NMR δ 3.42 (s, 3 H), 3.29 (s, 3 H), 2.42 (s, 1 H), 2.34 (d, J = 14.0 Hz, 1 H), 2.15 (dd, J = 2.0, 16.0 Hz, 1 H), 2.06 (d, J = 16.0 Hz, 1 H), 1.68 (dd, J = 2.0, 14.0, Hz, 1 H), 1.32 (s, 3 H), 1.18 (s, 9 H), 1.06 (s, 3), 1.02 (s, 3 H), 1.00 (s, 3 H); ^{13}C NMR δ 211.7, 103.9, 91.7, 84.0, 54.4, 51.7, 51.3, 49.0, 43.7, 41.7, 33.7, 31.8, 30.9, 27.7, 27.4, 27.1, 21.4; MS m/z 320 (M^+, 10), 116 (100); HRMS m/z 320.0104 (M^+, calcd for $C_{20}H_{32}O_3$ 320.0097). Data for **27c**: (only seen admixed with **26c**): ^{1}H NMR δ 3.25 (s, 3 H), 3.20 (s, 3 H), 3.07 (s, 1 H), 2.20–1.90 (m, 4 H), 1.17 (s, 9 H), 1.25 (s, 3 H), 1.24 (s, 3 H), 1.20 (s, 3 H), 1.11 (s, 3 H). Data for **30c**: IR (film) 1695, 1677, 1630, 1615 cm^{-1}; ^{1}H NMR δ 4.83 (dd, J = 3.9, Hz, 1 H), 4.79 (dd, J = 8.6, 9.4, Hz, 1 H), 2.86 (dd, J = 3.9, 8.6 Hz, 1 H), 2.54 (d, J = 17.4 Hz, 1 H), 2.32, (d, J = 16.0 Hz, 1 H), 2.29 (dd, J = 1.4, 17.4 Hz, 1 H), 2.14 (dd, J = 1.4, 16.0 Hz, 1 H), 1.34 (s, 3 H), 1.33 (s, 3 H), 1.1 (s, 3 H), 1.0 (s, 3 H), 0.9 (s, 9 H); ^{13}C NMR δ 190.8, 189.4, 159.0, 137.3, 118.6, 82.6, 51.7, 50.6, 42.7, 40.7, 35.0, 33.7, 30.1, 27.2, (3×), 26.8, 21.0, 20.8; UV (C_6H_{12}) λ_{max} 345 nm (log ϵ 3.62); MS m/z 288 (M^+, 36), 231 (100); HRMS m/z 288.2086 (M^+, calcd for $C_{19}H_{28}O_2$ 288.2089). Data for **36c**: ^{1}H NMR δ 6.16 (s, 1 H), 3.26 (s, 3 H), 3.19 (s, 3 H), 1.87 (s, 2 H), 1.82 (d, J = 14.4 Hz, 1 H), 1.75 (d, J = 14.4 Hz, 1 H), 1.4 (s, 6 H), 1.25 (s, 9 H), 0.99 (s, 3 H), 0.94 (s, 3 H); MS m/z 320 (M^+, 0), 262 ((M − 58)$^+$, 83), 116 (100). Anal. ($C_{20}H_{32}O_3$) C, H. Data for **38** (formed on attempted purification of **35c**): ^{1}H NMR δ 6.69 (s, 1 H), 1.99 (s, 4 H), 1.81 (s, 3 H), 1.74 (s, 3 H), 1.27 (s, 9 H), 0.90 (s, 6 H); MS m/z 230 (M^+, 95), 215 (100); HRMS m/z 230.0209 (M^+, calcd for $C_{20}H_{32}O_3$ 230.0203).

Entry 9. Irradiation for 4 h. Data *trans*-**39**: ^{1}H NMR δ 3.28 (s, 6 H), 2.8 (dd, J = 6.4, 11.3 Hz, 1 H), 2.45 (dd, J = 11.2, 11.2, 1 H), 2.4-1.7 (m, 6 H), 2.16 (dd, J = 6.4, 11.2, Hz, 1 H), 1.21 (s, 9 H); ^{13}C NMR δ 206.2, 104.5, 95.6, 77.0, 56.2, 50.5, 50.2, 48.4, 40.0, 31.6, 31.0 (3×), 27.4, 25.5; MS m/z 264 (M^+, 0), 88 (100). Anal. ($C_{16}H_{24}O_3$) C, H. Data for *cis*-**39**: ^{1}H NMR δ 3.32 (s, 3 H), 3.18 (s, 3 H), 2.57 (dd, J = 7.6, 9.6 Hz, 1 H), 2.47–2.25 (m, 4 H), 2.20–1.8 (m, 4 H), 1.22 (s, 9 H); ^{13}C NMR δ 211.3, 102.4, 92.6, 81.0, 49.7, 49.4, 49.2, 44.5, 38.7, 33.3, 31.2 (3×), 29.9, 27.5, 21.9; MS m/z 264 (M^+, 0), 88 (100). Anal. ($C_{16}H_{24}O_3$) C, H. Data for **40**: ^{1}H NMR δ 4.83 (m, 2 H), 3.26 (ddd, J = 2.2, 3.6, 22.8 Hz, 1 H), 3.14 (dddd, J = 1.1, 3.0, 3.0, 22.8 Hz, 1 H), 2.91 (m, 1 H), 2.64–2.54 (m, 2 H), 2.44–2.34 (m, 2 H), 2.19–1.89 (m, 2 H), 0.91 (s, 9 H); ^{1}H NMR (C_6D_6) δ 4.43 (dd, J = 4.0, 9.6 Hz, 1 H), 4.3 (dd, J = 9.6, 9.6 Hz, 1 H), 3.23 (ddd, J = 2.2, 3.6, 22.8 Hz, 1 H), 3.12 (dddd, J = 1.1, 3.0, 3.0, 22.8 Hz, 1 H), 2.43–1.58 (m, 7 H), 0.65 (s, 9 H); ^{13}C NMR δ 192.6, 179.8, 164.2, 129.8, 124.4, 82.9, 53.9, 50.9, 39.6, 37.1, 27.3 (3×), 27.0, 23.9; MS m/z 232 (M^+, 18), 175 (100); HRMS m/z 232.1438 (M^+, calcd for $C_{15}H_{20}O_2$ 232.1463).

Addition of 11 to 3a. Irradiation for 2.5 h. Isolation of **12a** by distillation; bp 95 °C (0.2 Torr) (87%). Data for **12a**: ^{1}H NMR δ 6.13 (s, 1 H), 3.45 (s, 3 H), 3.40 (s, 6 H), 3.28 (s, 3 H), 2.20–1.60 (m, 6 H), 1.23 (s, 9 H); ^{13}C NMR δ 130.4, 127.5, 116.2, 105.1, 99.0, 83.1, 79.7, 51.7, 50.9, 50.8, 49.5, 31.0, 29.8, 29.1, 27.8, 19.0; MS m/z 324 (M^+, 0), 234 ((M − 90)$^+$, 65), 133 (100). Anal. ($C_{18}H_{28}O_5$) C, H.

Addition of 11 to 3c. Irradiation for 4.5 h. Isolation of **12c** by distillation; bp 100 °C (0.2 Torr) (79%). Data for **12c**: ^{1}H NMR δ 6.16 (s, 1 H), 3.44 (s, 3 H), 3.40 (s, 3 H), 3.38 (s, 3 H), 3.22 (s, 3 H), 1.91 (s, 2 H), 1.83 (d, J = 15.0 Hz, 1 H), 1.69 (d, J = 15.0 Hz, 1 H), 1.24 (s, 9 H), 1.01 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR δ 128.8, 125.9, 116.6, 105.7, 98.8, 83.2, 80.1, 51.7, 51.0, 50.5, 49.1, 43.8, 42.1, 31.3, 31.0, 29.9, 27.8, 26.0; MS m/z 352 (M^+, 0), 262 ((M = 90)$^+$, 95), 133 (100). Anal. ($C_{20}H_{32}O_5$) C, H.

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