reaction analogous to the one in Scheme II, it is also expected to occur in other known ligand-promoted systems.[13] The implications for the OsO_4/alkaloid system are that low levels of alkaloid may be employed with nearly optimal enantioselectivity. Typical k_1/k_0 values lie in the range of 15–50 at 25 °C, and these increase substantially (up to ≈100 for styrene) at 0 °C. Further synthetic and mechanistic implications of ligand-accelerated catalysis are under current investigation.[14]

Acknowledgment. Financial support was provided by the National Science Foundation (Grant CHE-8303355) and Eli Lilly & Co. E.N.J., J.S.S., and K.B.S., respectively, thank the National Institutes of Health, the Royal Norwegian Council for Scientific and Industrial Research, and the John Simon Guggenheim Foundation for fellowships. Helpful discussions with Professors D. S. Kemp, S. Masamune, R. H. Grubbs, J. Halpern, and B. Bosnich are gratefully acknowledged. We are also grateful to Dr. H. U. Blaser of Ciba-Geigy for communication of his results prior to publication.

Supplementary Material Available: Derivation of eq 1 and 2 and Figures S1 and S2 containing plots of the concentration of **1** vs k_{obsd} and mole fraction of the major diol enantiomer (Figure S1) and k_{obsd}, k_f, and k_s (Figure S2) for the catalytic dihydroxylation of *trans*-stilbene (5 pages). Ordering information is given on any current masthead page.

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(12) Blaser and co-workers at Ciba-Geigy have recently observed a remarkably similar effect in *cinchona* alkaloid-modified heterogeneous platinum hydrogenation catalysts for the asymmetric reduction of α-keto esters. Blaser, H. U.; Jalett, H. P.; Monti, D. M.; Reber, J. F.; Wehrli, J. T. Heterogeneous Catalysis and Fine Chemicals. *Stud. Surf. Sci. Catal.* **1988**, *41*, 153.

(13) Finn, M. G.; Sharpless, K. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 8, p 247. Wynberg, H.; Staring, E. C. J. *J. Am. Chem. Soc.* **1982**, *104*, 166. Oguni, N.; Omi, T. *Tetrahedron Lett.* **1984**, *25*, 2823. Kitamura, M.; Suga, S.; Kawai, K.; Noyori, R. *J. Am. Chem. Soc.* **1986**, *108*, 6072. Smaardijk, A.; Wynberg, H. *J. Org. Chem.* **1987**, *52*, 135. Itsuno, S.; Sakurai, Y.; Ito, K.; Hirao, A.; Nakahama, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 395. Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551.

(14) Wai, J. S. M.; Markó, I.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* In press.

Reductive Cyclizations. The Electrochemical Generation of Cyclopropanes via the Double Intramolecular Cyclization of Initially Formed Vinyl Radicals

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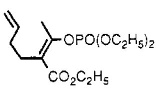
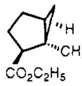
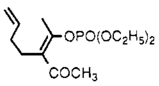
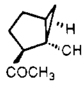
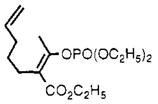
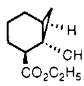
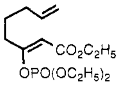
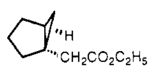
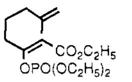
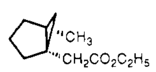
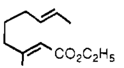
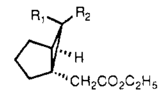
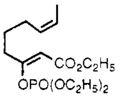
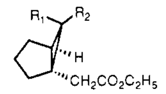
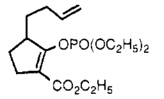
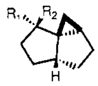
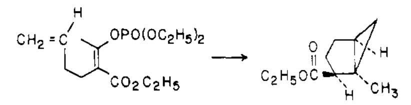
Numerous examples of the intramolecular addition of alkyl radicals to carbon–carbon double bonds have appeared in the literature.[1] However, much less is known about the analogous behavior of vinyl radicals.[2] The facile reduction of enol phosphates[3] and the alkylation[4] of β-dicarbonyl enol phosphates with dialkyl cuprates indicates that vinyl radicals derived from β-phosphonylated α,β-unsaturated carbonyl compounds can be generated with ease. However, when β-dicarbonyl enol phosphates were reductively alkylated in the presence of pendant olefinic linkages, no intramolecular addition occurred.[4,5] As part of our continuing interest in reductive cyclization reactions,[6] we have studied the electrochemical reduction of a series of 1,3-dicarbonyl enol phosphates bearing attached olefinic linkages. We now wish to report that, under controlled potential conditions, a variety of 1,3-dicarbonyl enol phosphates[7] were reduced to give reactive intermediates which, in a double cyclization process, gave bicyclo[*n*.1.0]alkanes where *n* was 3 or 4.

Table I. Products and Yields from the Double Reductive Cyclization of β-Dicarbonyl Enol Phosphates

example no.	starting material	product	% yield
(1)			58
(2)			55
(3)			38
(4)			63
(5)			53
(6)			51 R_1 = H, R_2 = CH_3 10 R_1 = CH_3, R_2 = H
(7)			41 R_1 = H, R_2 = CH_3 18 R_1 = CH_3, R_2 = H
(8)			26 R_1 = $CO_2C_2H_5$, R_2 = H 22 R_1 = H, R_2 = $CO_2C_2H_5$

In a typical procedure, the β-dicarbonyl enol phosphate, **1**, in



1 2

dimethylformamide, was added via syringe to an H-cell which contained a platinum gauze anode, a mercury pool cathode, a saturated calomel reference electrode, and a solution of 0.2 M tetra-*n*-butylammonium perchlorate in dimethylformamide, under a nitrogen atmosphere. The potential of the cathode was maintained at −2.05 V vs SCE, and **1** was added to the cathodic compartment at a rate sufficient to maintain the current between

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(1) For some pertinent reviews, see: Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206. Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon: Oxford, 1986. Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553. Stork, G. In *Selectivity: A Goal for Synthetic Efficiency*; Bartmann, W., Trost, B. M., Eds.; Verlag Chemie: Basel, 1984; p 281. Hart, D. J. *Science* **1984**, *223*, 883. Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

(2) Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1986**, *27*, 4529. Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525. Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3720. Marinovic, H. N.; Ramanathan, H. *Tetrahedron Lett.* **1983**, *24*, 1871. Knight, J.; Parsons, P. J.; Southgate, R. *J. Chem. Soc., Chem. Commun.* **1986**, 78. Padwa, A.; Nimmesgern, H.; Wong, G. S. K. *Tetrahedron Lett.* **1985**, *26*, 957. Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321.

(3) Ireland, R. E.; Pfister, G. *Tetrahedron Lett.* **1969**, 2145.

(4) (a) Alderdice, M.; Spino, C.; Weiler, L. *Tetrahedron Lett.* **1984**, *25*, 1643. (b) Sum, F. W.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1431. (c) Sum, P. E.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1475. Lombardo, D. A.; Weedon, A. C. *Tetrahedron Lett.* **1986**, *27*, 5555.

(5) Assuming that a vinyl radical was generated as an intermediate, these data indicate that alkylation is much more facile than intramolecular addition.

(6) Gassman, P. G.; Rasmy, O. M.; Murdock, T. O.; Saito, K. *J. Org. Chem.* **1981**, *46*, 5455.

(7) Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds. All compounds exhibited IR, ^{13}C NMR, and ^1H NMR spectra which were consistent with the assigned structures.

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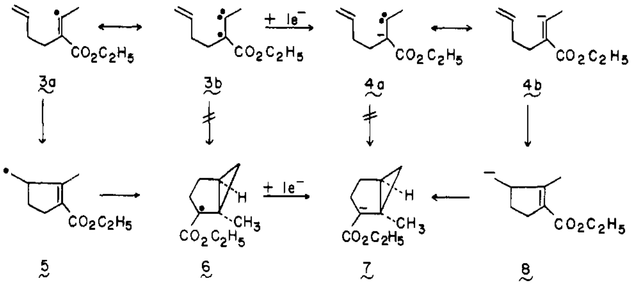
100 and 130 mA. After all of **1** had been added, the applied potential was increased to −2.30 V and maintained at this level until the current dropped below 10 mA. The reaction mixture was diluted with pentane and washed successively with 5% aqueous hydrochloric acid, water, and brine. After drying, the pentane solution was concentrated, and the product was isolated from the residue by medium pressure liquid chromatography to yield 58% of **2**.[8]

Table I lists the products and yields obtained for the reductive double cyclizations of a series of β-dicarbonyl enol phosphates. The first two examples from the table illustrate that both esters and ketones can function as the residual carbonyl containing group. The third example illustrates six-membered ring formation. Examples four and five show that the substitution patterns can be readily varied, while example eight illustrates the use of this cyclization for the formation of a tricyclic ester. Although the final protonation had been very stereoselective in examples one through three, example eight showed almost complete loss of stereoselectivity in the final addition of hydrogen, which indicates that protonation is comparably hindered from both faces of the cyclopentyl ring.

The mechanism of this reaction is complex and cannot be rigorously defined at this time. Structures **3** and **4** represent the transitory intermediates which would result from the one-electron and two-electron reductions, respectively, of **1**, coupled with the loss of the diethyl phosphate anion. The singlet carbene **4a** is a resonance structure of the vinyl anion **4b**, and **3b** is a resonance structure of **3a**. Several mechanistic possibilities exist. Cyclization of **3a** to give **5**, followed by a second cyclization to yield **6**, and subsequent reduction would produce **7**.[9] Carbene addition via **3b** would give **6** directly. Reduction of **3** would produce **4**, which could give **7** in either a two-step anionic process involving initial formation of **8** followed by intramolecular Michael addition or by an intramolecular carbene addition.



In order to establish that a singlet carbene addition was not involved, examples six and seven of Table I were run. These reactions demonstrated that the addition to the double bonds of the two starting materials occurred with the loss of stereochemical integrity. This would appear to exclude singlet carbenes such as **3a** or **4a** as reactive intermediates.[10] These two reactions illustrate that even though an intermediate is formed which allows isomerization to occur, the reactive intermediate must be short-lived since complete equilibration does not occur.[11-13]

In summary, an unprecedented electrochemical reduction of β-dicarbonyl enol phosphates[14] to bicyclo[*n*.1.0]alkanes has been developed.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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(8) In addition to 58% of **2**, approximately 19% of a four-electron reduction product (saturated monocarbonyl derivative) was obtained. The overall consumption of electrons was 2.4–3.0 Faradays per mole of β-dicarbonyl enol phosphate reduced in examples one through eight of Table I.

(9) Direct hydrogen abstraction by **6** to give **2** must also be considered as a possibility.

(10) This loss of stereochemistry requires the presence of an intermediate in which one bond has been formed to the pendant double bond to form a new intermediate, in which rotation can occur to give loss of stereospecificity. This is inconsistent with the addition of a singlet carbene to the double bond but would be compatible with radical cyclization, anionic attack, or addition of a triplet carbene.

(11) Double cyclization of vinyl radicals via intermediates analogous to **5** and **6** have been postulated previously in the literature.[2] However, *analogous cyclopropane derivatives have not been isolated.* In our examples, cyclopropane derivatives may be isolable due to the stabilization of both **6** and **7** by the attached carbonyl group.

(12) The reduction of **5** to **8** prior to the second cyclization reaction must also be considered. However, the short lifetime of the intermediate (ring closure competitive with bond rotation) makes this possibility unlikely.

(13) Examples six and seven of Table I also provide evidence against the formation of vinyl anions, such as **4b**, as intermediates in the double cyclization process. It has been noted that vinyl anions do not add intramolecularly to unactivated 1,2-disubstituted alkenes at a useful rate. For a pertinent discussion, see: Chamberlin, A. R.; Bloom, S. H.; Cervini, L. A.; Fotsh, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 4788. Bailey, W. F.; Patricia, J. J.; Nurmi, T. T. *Tetrahedron Lett.* **1986**, *27*, 1865.

(14) This reductive cyclization was not restricted to β-dicarbonyl enol phosphates. When the ethyl carbonate of the β-dicarbonyl enol corresponding to the β-dicarbonyl enol phosphate used in example five was electrochemically reduced under the normal reaction conditions, a 43% yield of the same product was obtained.

Absence of Conformational Dependence of Norrish II Biradical Lifetimes

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A few years ago we suggested, based on the direct observation of Norrish II biradicals from (gauche-locked) *cis*-1-benzoyl-2-benzhydrylcyclohexane and from (unconstrained but anti-biased) γ,γ-diphenylbutyrophenone,[1] that there was little or no dependence of lifetime of such 1,4 biradicals on conformation around the 2,3 bond. Subsequently, Johnston, Scaiano, Sheppard, and Bays[2] reported the photochemistry and transient spectroscopy of 1-benzoyl-2,2-dimethylcyclopropane (**1-H**) and diethyl analogue **1-Me**. Lifetimes reported for transients from **1-H** and **1-Me**, assigned as Norrish II biradicals, were in the range of 20 ns, a factor of 5 shorter than that for unconstrained but comparably substituted Norrish II biradicals in the same solvent (methanol). This result was presumed to reflect the short distance between the termini in biradicals **2-H** and **2-Me**, locked as eclipsed around the bond of interest, since it would have been consistent with the general proposition[3-5] that closer termini imply larger spin–orbit coupling, and thus faster intersystem crossing (isc) and shorter lifetimes. We now present evidence in favor of an alternate interpretation of the result, specifically that an adiabatic opening occurs prior to intersystem crossing of (cyclopropyldicarbinyl) biradicals **2-H** and **2-Me**. That, and not accelerated isc, is responsible for the attenuated lifetime. We have prepared the dibenzyl derivative **1-Ph**, which in contrast to **1-H** and **1-Me** affords a Norrish II biradical **2-Ph** with lifetimes very similar to those for an unconstrained model. Thermochemical considerations suggest that **2-H** and **2-Me** can, but **2-Ph** cannot, undergo adiabatic ring opening.

Photolysis through Pyrex of **1-Ph**, mp 74–75 °C,[6] affords two products in either methanol or benzene. One, a colorless oil, is

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(1) Caldwell, R. A.; Dhawan, S. N.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 6459.

(2) Johnston, L. J.; Scaiano, J. C.; Sheppard, J. W.; Bays, J. P. *Chem. Phys. Lett.* **1986**, *124*, 493.

(3) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(4) Mizuno, K.; Ichinose, N.; Otsuji, Y.; Caldwell, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5797. Barton, D. H. R.; Charpiot, B.; Ingold, K. U.; Johnston, L. J.; Motherwell, W. B.; Scaiano, J. C.; Stanforth, S. C. *J. Am. Chem. Soc.* **1985**, *107*, 3607.

(5) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 3618. Zimmt, M. B.; Doubleday, C., Jr.; Gould, I. R.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724.

(6) The synthesis of 1-Ph was analogous to that in ref 2 for **1-H** and **1-Me** and will be described elsewhere.

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