Rapid Regio- and Diastereoselective Paternò−Büchi Reaction of Alkyl Phenylglyoxylates

Shengkui Hu and Douglas C. Neckers*

Center for Photochemical Sciences,[1] Bowling Green State University, Bowling Green, Ohio 43403

Received August 5, 1996[⊗]

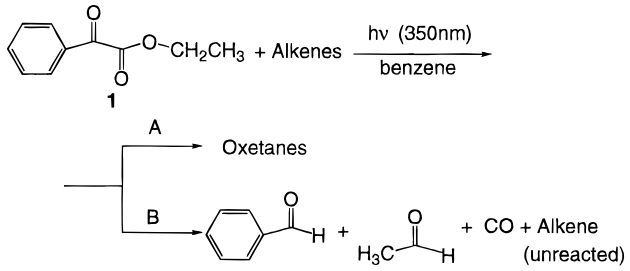
Triplet excited states of alkyl phenylglyoxylates react rapidly ($k = 9.4 \times 10^9$ M^{-1} s^{-1}) with electron rich alkenes forming oxetanes with high regio and stereoselectivity. The well-known intramolecular γ-hydrogen abstraction (Norrish type II) cannot compete. When less electron-rich alkenes are used, the Norrish type II reaction becomes competitive. Intramolecular Paternò−Büchi reactions predominate in those alkyl phenylglyoxylates containing properly situated electron-rich alkene groups. The regioselectivity of this reaction is explained by the stability of the intermediate 1,4-biradical. The appropriate conformation at the instant of intersystem crossing determines the stereoselectivity of the products. The priority of the Paternò−Büchi over the Norrish type II reaction is understood by considering the conformation of phenylglyoxylate esters.

Introduction

[2 + 2] Photocycloaddition of carbonyl compounds to ethylenes yielding oxetanes (Paternò−Büchi reaction) is well known.[2] In our recent reinvestigation of the photochemical reactions of alkyl phenylglyoxylates,[3] we found that methyl phenylglyoxylate undergoes a rapid Paternò−Büchi reaction ($k = 9.4 \times 10^9$ M^{-1} s^{-1}) with high chemical yield (92%). We have now carried out a more complete study on the Paternò−Büchi reaction of phenylglyoxylates and on its competition with the well-understood Norrish type II reaction.

The Paternò−Büchi reaction has been widely used in synthetic organic chemistry to prepare oxetane-containing chiral natural products or as a route to photoaldolization.[4] Scharf and co-workers used the Paternò−Büchi reaction of chiral alkyl phenylglyoxylates for the determination of isoinversion points.[5] In the study we report herein, we have carried out both inter- and intramolecular Paternò−Büchi reactions of alkyl phenylglyoxylates and observed the interplay of Paternò−Büchi and Norrish type II reactions when different alkenes are used.

Scheme 1



Results and Discussion

Ethyl phenylglyoxylate (**1**) was irradiated in the presence of an equimolar amount of a series of alkenes in benzene solution (0.01 M). Two different reactions proceed depending on the structure of the alkene used; see Scheme 1. Pathway A is the Paternò−Büchi cycloaddition reaction forming oxetanes and occurs rapidly with electron-rich alkenes. Pathway B is the Norrish type II photolysis of **1** wherein the alkene is recovered unchanged. The results of reactions using different alkenes are accumulated in Table 1.

We intentionally varied the structure of the alkenes used in this study from more to less electron rich (Table 1). With electron-rich alkenes (enol ethers or polyalkyl-substituted alkenes **2**−**8**), the Paternò−Büchi reaction dominates, and no products from Norrish type II reactions are observed. With monosubstituted alkenes (**10**, **11**), no Paternò−Büchi reaction is observed. Further reducing the electron richness of the alkenes (alkenes **12**−**15**) produces similar results. This confirms that the S_1 state of ethyl phenylglyoxylate is too short lived to react via a Paternò−Büchi pathway. The regio- and stereoselectivity displayed in the Paternò−Büchi reaction of phenylglyoxylate is pure ^1T (n,π^*)-state photochemistry. Alkene **9** is unreactive in the Paternò−Büchi reaction contrary to **6**−**8** because **9** is more flexible. Besides its electron richness, structural rigidity influences the alkene's reactivity in the Paternò−Büchi reaction.

Alkyl phenylglyoxylates with internal double bonds, **23** and **24**, were synthesized and irradiated in benzene solution (0.01 M). Compound **25** and its photochemistry have been reported.[6] These results are collected in Table 2.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1997.

(1) Contribution No. 284 from the Center for Photochemical Sciences.

(2) For reviews, see: (a) Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301−423. (b) Jones, G., II. *Org. Photochem.* **1981**, *5*, 1−122. (c) Carless, H. A. J. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1984; pp 425−487. (d) Porco, J. A., Jr.; Schreiber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Plenum: New York, 1991; Vol. 5, pp 151−192. (e) Griesbeck, A. G. In *Handbook of Photochemistry and Photobiology*; Horspool, W. A., Song, P.-S., Eds.; CRC Press: Boca Raton, 1994. (f) Turro, N. J. *Modern Molecular Photochemistry*; University Book: 1991; pp 432−452. (g) Neckers, D. C. *Mechanistic Organic Photochemistry*; Reinhold: New York, 1967; pp 131−138.

(3) (a) Huyser, E. S.; Neckers, D. C. *J. Org. Chem.* **1964**, *29*, 276−278. (b) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1996**, *61*, 6407−6415.

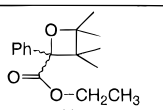
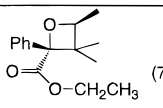
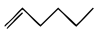
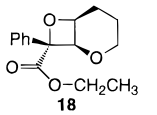
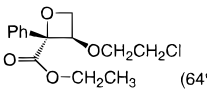
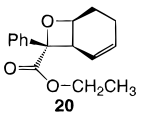
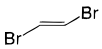
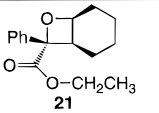
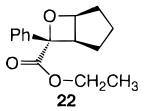
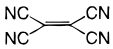
(4) (a) Mattay, J.; Buchkremer, K. *Helv. Chim. Acta* **1988**, *71*, 981−987. (b) Mattay, J.; Buchkremer, K. *Heterocycles* **1988**, *27*, 2153−2165. (c) Araki, Y. *J. Chem. Soc., Perkin Trans. 1* **1981**, 12. (d) Schreiber, S. L. *Science* **1985**, *227*, 857−863. (e) Schreiber, S. L. *J. Am. Chem. Soc.* **1983**, *105*, 660−661. (f) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* **1984**, *106*, 4186−4188. (g) Schreiber, S. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1984**, *106*, 7200−7202. (h) Nehrings, A.; Scharf, H.-D.; Runsink, J. *Angew. Chem.* **1985**, *97*, 882. *Angew Chem., Int. Ed. Engl.* **1985**, *24*, 877−879. (i) Weuthen, M.; Scharf, H.-D.; Runsink, J.; Vassen, R. *Chem. Ber.* **1988**, *121*, 971−976. (j) Kozluk, T.; Zamojski, A. *Tetrahedron* **1983**, *39*, 805−810.

(5) (a) Buschmann, H.; Scharf, H.-D.; Hoffmann, N.; Esser. P. *Angew. Chem.* **1991**, *103*, 480; *Angew Chem., Int. Ed. Engl.* **1991**, *30*, 477−515. (b) Buschmann, H.; Scharf, H.-D.; Hoffmann, N.; Plath, M. W.; Runsink, J. *J. Am. Chem. Soc.* **1989**, *111*, 5367−5373.

(6) Kraus, G. A.; Wu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 8705−8707.

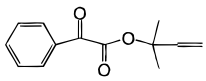
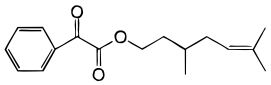
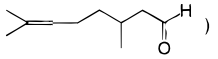
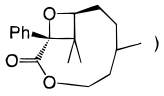
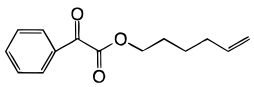
S0022-3263(96)01505-8 CCC: $14.00

Table 1. Results of Ethyl Phenylglyoxylate Reactions with Different Alkenes

Alkenes react via Pathway **A**		Alkenes react via
Alkenes	Oxetanes* and Yield	Pathway **B**
 **2**	 (92%) **16**	 **9**
 **3**	 (70%) **17**	 **10**
 **4**	 (70%) **18**	 **11**
 **5**	 (64%) **19**	 **12**
 **6**$^{\Delta}$	 (81%) **20**	 **13**
 **7**	 (76%) **21**	 **14**
 **8**	 (65%) **22**	 **15**

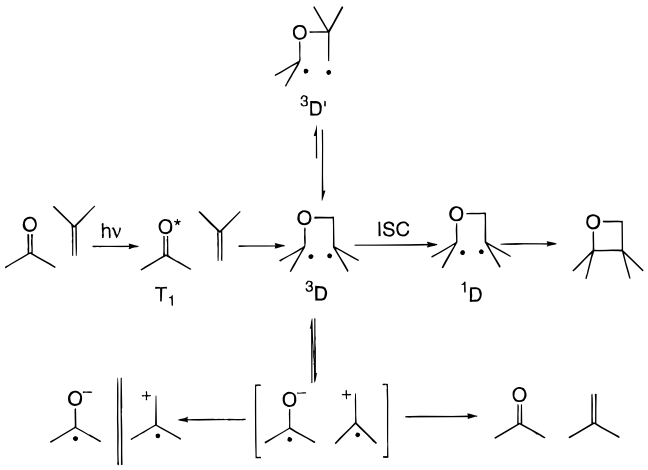
* Isolated as mixture of two enantiomers. Further separation was not attempted in this study.
$^{\Delta}$The molar amount of **6** used is 1/2 of that of **1**.

Table 2. Alkyl Phenylglyoxylates with Internal Double Bond and Their Photoreaction Results

Compounds	Photoreaction Results
 **23**	No products from either Norrish Type II or Paternò-Büchi reaction
 **24**	25% Norrish Type II (from isolated ) 70% Paternò-Büchi reaction (from isolated ) **26** (mixture of two enantiomers)
 **25**	Only Norrish Type II products were observed

Compound **23** does not undergo a Norrish type II reaction since no γ-hydrogen is available, neither does it undergo a Paternò−Büchi reaction (the alkene portion is insufficiently electron rich and the two functional groups are too close together). Compound **24** undergoes both the Norrish type II process and the intramolecular Paternò−Büchi reaction with the Paternò−Büchi reaction playing a major role. No intermolecular Paternò−Büchi reaction is observed for **24**. The intramolecular Paternò−Büchi reaction is also absent for compound **25** since its alkene functionality is not sufficiently electron rich.

Scheme 2



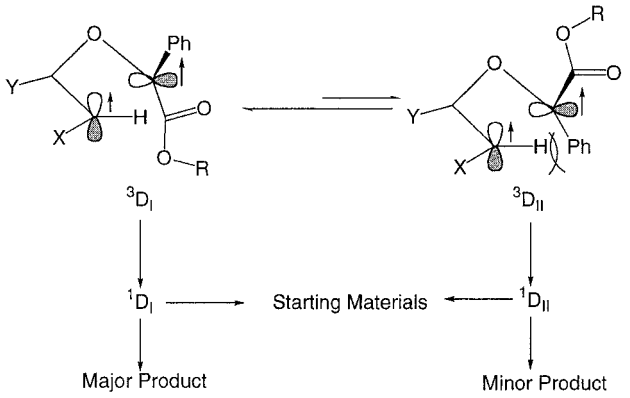
The major products of the Paternò−Büchi reactions (Tables 1 and 2) show both high regio- and stereoselectivity. In most cases, regioselectivities are higher than 95%. This can be understood by considering the mechanism of the Paternò−Büchi reaction as shown in Scheme 2. The intermediate 1,4-biradical was detected by picosecond absorption spectroscopy.[7] When the alkene used is asymmetric, the most stable 1,4-biradical (^{3}D rather than ^{3}D′) is formed to furnish major products regioselectively.

The stereoselectivity of the Paternò−Büchi reaction is attributed to the conformational memory effects during the intersystem crossing (ISC) of the triplet 1,4-biradical.[8] Because of the relatively long lifetime of the triplet biradicals as compared to singlet biradicals, a decrease in stereoselectivity should be observed in photoreactions via triplet biradicals. On the other hand, spin−orbit coupling (SOC),[9] the dominating factor that determines lifetime of the 1,4-biradical, is strongly dependent on the geometry of the triplet biradical. The triplet 1,4-biradical has to assume a specific conformation before ISC. Because of the very short lifetime of the resulting singlet 1,4-biradical, the appropriate ISC conformation is reflected in the stereoselectivity of photoproducts.

The Salem−Rowland rules[10] governing the mechanisms of SOC require the conservation of total angular momentum. This can be achieved when the axes of the p orbitals at the radical centers are oriented perpendicular to each other. A plausible explanation for the stereoselectivity of product formation is depicted in Scheme 3. Two conformations of the triplet radical (^3D_I and $^3D_{II}$) can fulfill the Salem−Rowland requirement and are able to ISC to singlet states (^1D_I and $^1D_{II}$). ^1D_I and $^1D_{II}$ can dissociate to the starting materials or cyclize forming oxetanes. Triplet $^3D_{II}$ is less stable due to steric

(7) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 3819−3822.
(8) Griesbeck, A. G.; Mauder, H.; Stadtmüller, S. *Acc. Chem. Res.* **1994**, *27*, 70−75.
(9) For a review, see: Michl, J.; Klessinger, M. *Excited States and Photochemistry of Organic Molecules;* VCH: New York, 1995; pp 219−228.
(10) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.
(11) Griesbeck, A. G.; Stadtmüller, S. *J. Am. Chem. Soc.* **1990**, *112*, 1281.

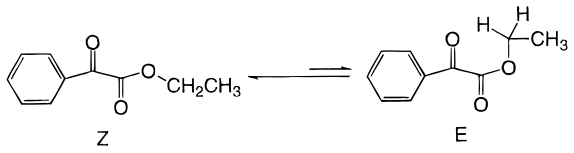
Scheme 3



repulsion[11] and is thus depopulated. The lifetimes of ^1D_I and $^1D_{II}$ are too short to allow significant rotation around the C−O bond. Thus, the proper conformations assumed by the triplets (^3D_I,$^3D_{II}$) are preserved in the photoproducts. This allows the prediction of the conformations of the products in Tables 1 and 2. Semiempirical calculations (AM1) show that the major products are about 0.5−1 kcal/mol more unstable than the corresponding minor products. These results show that the stereoselectivity observed is contrathermodynamic control and SOC-controlled spin inversion is the essential factor determining the stereochemistry of products.

In general, when an electron-rich alkene is present, the triplets of the alkyl phenylglyoxylate undergo the Paternò−Büchi reaction in lieu of the Norrish type II photolysis. The reaction rate of the Norrish type II reaction for methyl phenylglyoxylate is estimated to be at least 4 orders of magnitude lower than that of its photocycloaddition with alkene **1**.[3b] The low reaction rate of the Norrish type II of methyl phenylglyoxylate is not successfully attributed to either the nature of the γ-hydrogen or the geometry of the transition state.[12] We found, however, that the low rate of the Norrish type II reaction of phenylglyoxylate esters can be successfully attributed to the conformation of these α-keto esters. In principle, normal esters might exist in either *E* or *Z* conformations.[13] *Z* conformers are found to be 5−6 kcal/mol more stable than the corresponding *E* conformers.[14] We performed geometry optimization on ethyl phenylglyoxylate[15] using the AM1 semiemperical method[16] and found that the *E* conformer, which exists in the required geometry for intramolecular hydrogen abstraction,[17] is 4.37 kcal/mol higher in energy than the *Z* conformer (Scheme 4).

Scheme 4



Therefore, the Norrish type II reaction is only possible in the excited state of the *E* conformer, which is populated by only about 1%[18] of the molecules in solution. This explains why the Norrish type II rate constant of phenylglyoxylates is 2 orders of magnitude smaller than that of similar phenyl ketones.[3b] Since Paternò−Büchi reactions can occur in both *E* and *Z* conformers, the low population of the *E* conformer does not effect the rate of the Paternò−Büchi reaction.

In summary, phenylglyoxylates react with electron-rich alkenes forming oxetanes with predictable stereochemistry. The priority of the Paternò−Büchi reaction over Norrish type II reaction can be explained by the unfavorable Norrish type II conformation of phenylglyoxylates.

Experimental Section

Materials. Benzene (Aldrich) was dried over sodium under argon. Ethyl phenylglyoxylate (**1**) was obtained from Aldrich and purified by column chromatography before use. Other chemicals were used as received. NMR spectra were taken with either a Varian Gemini 200 NMR spectrometer or a Varian Unity Plus 400 NMR spectrometer. Chemical shifts are in ppm with TMS as the internal standard. GC/MS were taken on a Hewlett-Packard 5988 mass spectrometer coupled to a HP 5880A GC, interfaced to a HP 2623A data processor. Infrared spectra were taken with a Galaxy series 6020 FTIR spectrometer. Thin-layer chromatography was performed with Whatman silica gel coating TLC plates. Products are isolated by flash column chromatography using Aldrich silica gel (60 Å, 70−270 mesh). The elution solvents were indicated following the compound name. Semiempirical calculations were performed with a Silicon Graphics Indigo using the package Spartan.[19] HRMS were obtained from the University of Illinois at Urbana−Champaign. General procedures for irradiating samples and isolating photoreaction products were reported earlier.[3b]

2-(Ethoxycarbonyl)-2-phenyl-3,3,4,4-tetramethyloxetane (16) (mixture of two enantiomers): hexanes:ethyl acetate = 20:1; slightly yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (s, 3H), 1.26 (s, 3H), 1.29 (t, J = 7.6 Hz, 3H), 1.33 (s, 3H), 1.45 (s, 3H), 4.15−4.31 (m, 2H), 7.25−7.40 (m, 3H), 7.55−7.70 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.17, 22.22, 22.45, 25.44, 25.60, 47.01, 61.03, 85.08, 88.30, 126.08, 127.32, 127.54, 139.30, 172.72; MS 77 (12), 84 (15), 105 (100), 158 (5.1), 189 (22), 204 (1.3, M − 58); IR (neat) 2971.29, 2928.84, 1744.19, 1724.69, 1481.79, 1447.06, 1373.74; HRMS *m/e* calcd 262.1566, found 262.1569.

2-(Ethoxycarbonyl)-2-phenyl-3,3,4-trimethyloxetane (17) (mixture of two enantiomers): hexanes:ethyl acetate = 20:1; clear oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.78 (s, 3H), 1.23 (d, J = 6.6 Hz, 3H), 1.30 (s, 3H), 1.30 (t, J = 7.0 Hz, 3H), 4.25 (dd, J = 7.0 Hz, 1.4 Hz, 2H), 4.68 (q, J = 6.6 Hz, 1H), 7.20−7.40 (m, 3H), 7.50−7.63 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.24, 17.06, 19.70, 25.39, 45.97, 61.24, 83.55, 90.00, 125.92, 127.32, 127.37, 138.78, 172.27; MS 77 (44.5), 91 (5.1), 105 (100), 158 (3.6), 175 (21.3), 179 (19.6), 204 (1.0, M − 44); HRMS *m/e* calcd 248.1413, found 248.1412.

***endo*-8-(Ethoxycarbonyl)-8-phenyl-2,7-dioxabicyclo-[4.2.0]octane (18) (mixture of two enantiomers)**: hexanes:

(12) Pappas, S. P.; Alexander, J. E.; Zehr, R. D., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 6927−6931.

(13) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1994; Chapter 10.

(14) (a) Blom, C. E.; Günthard, H. H. *Chem. Phys. Lett.* **1981**, *84*, 267−271. (b) Ruschin, S.; Bauer, S. H. *J. Phys. Chem.* **1980**, *84*, 3061−3065. (c) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935−5943. (d) Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1. (e) Allinger, N. L.; Chang, S. H. M. *Tetrahedron* **1977**, *33*, 1561. (f) Radom, L.; Lathan, W. A.; Hetre, W. J.; Pople, J. A. *Austr. J. Chem.* **1972**, *25*, 1601.

(15) All 14 alkyl phenylglyoxylates involved in the earlier study (ref 3b) have been studied. Similar results are obtained.

(16) AM1 was chosen because it gives the most stable conformer structure in excellent agreement with single-crystal X-ray diffraction of phenylglyoxylate. Runsink, J.; Koch, H.; Nehrings, A.; Scharf, H.-D.; Nowack, E.; Hahn, T. *J. Chem. Soc., Perkin Trans. 2* **1988**, 49−55.

(17) Wagner, P. J.; Meador, M. A.; Zhou, B.; Park, B-S. *J. Am. Chem. Soc.* **1991**, *113*, 9630−9639. Wagner, P. J.; Zhou, B.; Hasegawa, T.; Ward, D. L. *J. Am. Chem. Soc.* **1991**, *113*, 9640−9654. Gudmundsdottir, A. D.; Lewis, T. J.; Randall, L. H.; Scheffer, J. R.; Rettig, S. J.; Trotter, J.; Wu, C.-H. *J. Am. Chem. Soc.* **1996**, *118*, 6167−6184.

(18) Obtained by taking the energy difference in solution is half of that in gaseous phase (Grindley, T. B. *Tetrahedron Lett.* **1982**, *23*, 1757) and utilizing Boltzmann distribution law, $X_E/X_Z = \exp(\Delta H/RT)$.

(19) Spartan version 4.0.1, Wavefunction Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92715.

ethyl acetate = 20:1−5:1; clear oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.29 (t, J = 6.8 Hz, 3H), 1.76−1.88 (m, 2H), 1.94−2.06 (m, 2H), 3.81 (s, 1H), 3.94 (t, J = 5.8 Hz, 2H), 4.20−4.32 (m, 2H), 6.21 (s, 1H), 7.24−7.38 (m, 3H), 7.52−7.61 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.30, 21.97, 65.47, 80.28, 98.40, 114.48, 126.91, 127.76, 127.87, 139.62, 143.94, 174.22; MS 55 (11.1), 77 (17.3), 84 (100), 91 (3.2), 105 (34.9), 143 (1.2), 189 (14.1, M − 73); HRMS *m/e* calcd 262.1204, found 262.1205.

2-(Ethoxycarbonyl)-2-phenyl-3-(2′-chloroethoxyl)oxetane (19) (mixture of two enantiomers): hexanes:ethyl acetate = 1:2; yellowish oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.29 (t, J = 7.2 Hz, 3H), 3.32 (m, 2H), 3.66 (t, J = 5.2Hz, 2H), 4.28 (q, J = 7.2Hz, 2H), 4.49 (t, J = 7.0 Hz, 1H), 4.76 (t, J = 7.0 Hz, 1H), 4.92 (t, J = 7.0 Hz, 1H), 7.22−7.39 (m, 3H), 7.48−7.63 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.01, 42.14, 63.93, 70.07, 73.57, 77.99, 92.98, 125.78, 128.25, 128.45, 134.43, 171.79; MS 43 (23.3), 63 (19.9), 77 (26.8), 105 (100), 106 (60.4), 108 (17.6), 146 (5.9), 204 (4.6), 254 (1.8, M − 30); HRMS *m/e* calcd 284.0817, found 284.0815.

***endo*-8-(Ethoxycarbonyl)-8-phenyl-7-oxabicyclo[4.2.0]-oct-2-ene (20) (mixture of two enantiomers)**: hexanes:ethyl acetate = 10:1; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 6.8 Hz, 3H), 1.92−2.15 (m, 4H), 3.82 (t, J = 11.2 Hz, 1H), 4.24 (m, 2H), 5.28 (m, 1H), 5.50 (m, 1H), 5.82 (m, 1H), 7.25 (m, 1H), 7.32 (m, 2H), 7.37 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.07, 19.92, 25.19, 41.19, 61.73, 75.69, 89.28, 123.24, 125.09, 126.90, 127.21, 127.39, 127.70, 131.70, 137.71, 173.65; MS 51 (13.2), 77 (58.4), 79 (56.9), 80 (100), 105 (70.3), 180 (15.1), 185 (6.2, M − 73); HRMS *m/e* calcd for $C_{13}H_{13}O$ 185.0966, found 185.0966.

***endo*-8-(Ethoxycarbonyl)-8-phenyl-7-oxabicyclo[4.2.0]-octane (21) (mixture of two enantiomers)**: hexanes:ethyl acetate = 10:1; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 2H), 1.04 (m, 2H), 1.25 (t, J = 7.2 Hz, 3H), 1.40 (m, 2H), 1.59 (m, 2H), 3.33 (dt, J = 6.4, 8.4 Hz, 1H), 4.23 (m, 2H), 5.01 (m, 1H), 7.29 (m, 1H), 7.36 (m, 2H), 7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.09, 19.07, 20.33, 28.10, 31.57, 40.75, 61.60, 75.38, 87.67, 125.31, 127.53, 128.04, 137.83, 174.22; IR (neat) 3003.90, 2936.56, 2870.96, 1728.75, 1450.92, 1257.97, 1.34.16; MS 51 (2.6), 77 (15.8), 91 (2.8), 105 (100), 187 (23.5), 214 (0.1, M − 46); HRMS calcd for $C_{13}H_{15}O$ 187.1123, found 187.1122.

***endo*-7-(Ethoxycarbonyl)-7-phenyl-6-oxabicyclo[3.2.0]-heptane (22) (mixture of two enantiomers)**: petroleum ether:ethyl acetate = 10:1; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J = 7.2 Hz, 3H), 1.04 (m, 2H), 1.31 (m, 2H), 1.43 (m, 1H), 1.51 (m, 1H), 1.64 (m, 1H), 2.00 (m, 1H), 3.59 (dt, J = 5.2, 0.8 Hz, 1H), 4.21 (m, 2H), 5.35 (m, 1H), 7.29 (m, 1H), 7.36 (m, 2H), 7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.02, 24.07, 27.07, 33.65, 47.02, 61.60, 84.20, 86.10, 125.32, 127.42, 127.80, 136.88, 174.04; IR (neat) 3060.04, 2959.71, 2878.68, 1728.75, 1447.06, 1242.54, 1080.47, 1022.58; MS 51 (4.3), 67 (5.5), 77 (20.9), 91 (3.1), 105 (100), 115 (7.4), 173 (30.0), 174 (4.1, M − 72); HRMS calcd for $C_{12}H_{13}O$ 173.0966, found 173.0966.

1′,1′-Dimethyl-2′-propenyl Benzoylformate (23). Benzoylformyl chloride was synthesized as reported.[20] Equimolar amounts of 2-methyl-3-buten-2-ol and benzoylformyl chloride were dissolved in chloroform. Triethylamine was added dropwise over 1 h. The resulting solution was stirred for 4 h and washed with saturated $NaHCO_3$ solution and water each for three times. The title compound was obtained in 82% yield after column chromatography (hexanes:ethyl acetate = 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (m, 3H), 1.80 (m, 3H), 4.89 (dt, J = 7.2, 0.4 Hz, 2H), 5.47 (tq, J = 7.2, 0.4 Hz, 1H), 7.50 (m, 2H), 7.63 (m, 1H), 7.99 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.12, 25.77, 62.95, 117.30, 128.82, 129.99, 132.50, 134.79, 141.11, 163.83, 186.39; MS 41 (44.8), 69 (67.4), 77 (63.5), 105 (100), 218 (0.01, M); HRMS *m/e* calcd 218.0943, found 218.0944.

3′,7′-Dimethyl-6′-octenyl Benzoylformate (24). The title compound was synthesized by the DCC reaction described earlier:[3b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, J = 6.4 Hz, 3H), 1.19−1.27 (m, 2H), 1.35−1.41 (m, 1H), 1.59 (s, 3H), 1.66 (s, 3H), 1.80−1.86 (m, 2H), 1.95−2.04 (m, 2H), 4.44 (t, J = 5.8 Hz, 2H), 5.08 (tq, J = 8.0, 1.6 Hz, 1H), 7.49 (t, J = 7.2 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 8.01 (d, J = 7.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.57, 19.27, 25.28, 25.62, 29.32, 35.20, 36.83, 64.73, 124.31, 128.81, 129.92, 131.40, 132.43, 134.79, 163.91, 186.37; MS 41 (24.1), 56 (29.3), 77 (31.4), 95 (15.8), 105 (100), 123 (10.0), 138 (8.7), 155 (3.4), 224 (8.1), 270 (2.3), 288 (0.3, M); HRMS *m/e* calcd 288.1725, found 288.1724.

6,10,10-Trimethyl-2-oxo-1-phenyl-3,11-dioxabicyclo-[7.1.1]nonadecane (26) (mixture of two enantiomers): hexanes:ethyl acetate = 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (d, J = 6.8 Hz, 3H), 1.24 (s, 3H), 1.37 (m, 1H), 1.40 (s, 3H), 1.59 (m, 2H), 1.67 (m, 2H), 2.13 (m, 2H), 2.92 (dd, J = 1.2Hz, 0.4Hz, 1H), 3.78 (m, 1H), 4.77 (m, 1H), 7.29 (m, 2H), 7.37 (m, 2H), 7.54 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.82, 21.07, 23.88, 30.23, 30.49, 30.74, 31.41, 52.63, 66.13, 82.52, 84.16, 125.94, 127.33, 127.89, 141.91, 171.46; MS 77 (16.3), 105 (100), 159(13.2), 244 (3.3), 288 (0.5, M); HRMS *m/e* calcd 288.1725, found 288.1727.

Acknowledgment. We thank the National Science Foundation (Grant Nos. DMR-9013109 and CHE-9302619) and the Office of Naval Research (Grant No. N00014-91-J-1921) for financial support.

Supporting Information Available: NMR spectra for **16**−**24** and **26** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9615054

(20) Ottenheijm, H. C. J.; De Man, J. H. M. *Synthesis* **1975**, 163−164.