Nucleophilic Cyclopropanation Reactions of Unsaturated Acylphosphoranes

Manning P. Cooke, Jr.,* and John-Yan Jaw

Department of Chemistry, Washington State University, Pullman, Washington 99164

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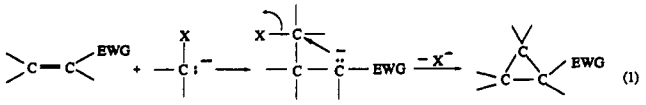
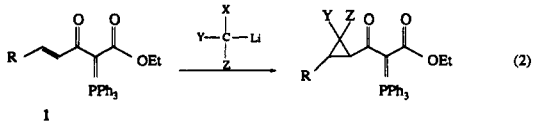
The cyclopropanation of activated olefins through sequential Michael addition and intramolecular alkylation reactions is well-known (eq 1). Most commonly encountered are reactions of phosphorus- and sulfur-based ylides[1] and Darzen-type reactions employing stabilized α-halo carbanions or enolates.[2] Polyhalocarbanions (carbenoids), which are usually stable only at low temperatures, are rarely useful in nucleophilic cyclopropanation reactions[3] of electron-deficient olefins owing to the mild conditions necessary for their preservation and to their facile reactions with the carbonyl groups often employed in olefin activations.[4] On the other hand, their utility in the cyclopropanation of electron-rich olefins through decompositions to carbene intermediates is well developed.[5]



(1)

We have previously shown that unsaturated acylphosphoranes undergo charge-directed conjugate addition reactions with a wide range of nucleophiles[6] and that such reactions may be used to initiate highly efficient intramolecular cyclization reactions leading to three-,[7] five-, and six-membered[8] rings.[9] Product acylphosphoranes may be subsequently transformed into a variety of carboxyl[6,10] and ketone[11] derivatives. These Michael acceptors seemed ideally suited for nucleophilic cyclopropanation reactions insomuch as their charge-protected olefin-activating carbonyl groups are highly resistant to 1,2-carbonyl addition reactions. Herein we report the results of a study of such reactions (eq 2). The results of the addition of a number



(2)

1

of (halomethyl)lithium reagents to unsaturated acylphosphoranes (1) are shown in Table I.

In general, the additions of (halomethyl)lithium reagents at low temperatures to unsaturated acceptors followed by warming to ensure cycloalkylation resulted in excellent yields of cyclopropyl derivatives. Only in the cases involving (trichloromethyl)lithium (entries 2 and 8) were Michael additions not followed by ring closures. A similar resistance of the trichloromethyl group to such cycloalkylation reactions has previously been noted.[12]

The addition–cycloalkylation reactions of (dihalomethyl)lithium reagents likewise gave good yields of cyclopropyl derivatives (entries 3–5) with unsubstituted acceptor **1a**. Separable mixtures of trans and cis isomers resulted in which the trans isomers (vide infra) heavily predominated in each case as would be predicted from a least sterically encumbered transition-state model for the cycloalkylation step. Lower yields resulted with β-substituted acceptor **1b** (entries 9 and 10), however, and the products, **11** and **12**, while predominately one isomer,[13] respectively, contained a small amount of an inseparable isomer in each case.

The addition of (tribromomethyl)lithium to diene acceptor **1c** is especially noteworthy in that cyclopropanation occurs at the electron-deficient double bond in keeping with the proposed nucleophilic addition mechanism outlined in eq 1. An alternate pathway involving dibromocarbene would likely have given cyclopropanation at the electron-rich trisubstituted double bond.

While [chloro(trimethylsilyl)methyl]lithium generated, under conditions known to discourage carbene formation,[14] readily cyclopropanated **1a** (entry 6), a number of other substituted (halomethyl)lithium reagents (PhCHXLi[15] (X = Cl, Br), CH_2=CHCHXLi[16] (X = Cl, Br), ClCH(CN)Li,[17] LiCXRCOOEt[2f] (R = Me, H; X = Br, Cl)) gave essentially no reaction with **1a**. These stabilized donors are apparently unable to undergo Michael addition reactions with our ylide acceptors.

While stereochemical assignments of product cyclopropyl derivatives could be made on the basis of transition-state models involving the usual stereoelectronic considerations[18] as well as precedents found in related ylide cyclopropanation reactions,[19] in many cases assignments followed readily from NMR data. Compound **4** is assigned as the trans isomer based on the downfield chemical shift

(1) Helquist, P. In *Comprehensive Organic Synthesis*; Trost, B., Fleming, I., Eds.; Pergamon Press: New York, 1991; p 986 and references therein.

(2) (a) Bonavent, G.; Causse, M.; Guitard, M.; Fraisse-Jullien, R. *Bull. Chim. Soc. Fr.* **1964**, 2462. (b) Jonczky, A.; Makosza, M. *Synthesis* **1976**, 387. (c) Jonczyk, A.; Makosza, M. *Synthesis* **1976**, 387. (d) Trost, B. M.; Frazee, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 6124. (e) Sanel, S.; Langbeleim, M. *J. Chem. Soc., Chem. Commun.* **1977**, 593. (f) Fauduet, H.; Burgada, R. *Synthesis* **1980**, 642. (g) Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691. (h) Hamdouchi, C. *Tetrahedron Lett.* **1992**, *33*, 1701.

(3) (a) Nanjo, K.; Suzuki, K.; Sekiya, M. *Chem. Lett.* **1977**, 553. (b) Baird, M. S.; Gerrard, M. E. *Tetrahedron Lett.* **1985**, *26*, 6353.

(4) (a) Cainelli, G.; Ronchi, A.; Bertini, F.; Grasselli, P.; ZuBiani, G. *Tetrahedron* **1971**, *27*, 6109. (b) Villieras, J.; Rambaud, M. *Synthesis* **1980**, 644.

(5) (a) Hoeg, D. F.; Lusk, D. I.; Crumbliss, A. L. *J. Am. Chem. Soc.* **1965**, *87*, 4147. (b) Kobrich, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 41. (c) Kobrich, G. *Ibid.* **1972**, *11*, 473. (d) Villieras, J.; Bacquet, C.; Masure, D.; Normant, J. F. *J. Organomet. Chem.* **1973**, *50*, C7. (e) Villieras, J.; Bacquet, C.; Normant, J. F. *Bull. Soc. Chim. Fr.* **1975**, 1797. (f) Villieras, J.; Perriot, P.; Normant, J. F. *Ibid.* **1977**, 765.

(6) Cooke, M. P., Jr.; Goswami, R. *J. Am. Chem. Soc.* **1977**, *99*, 642.

(7) Cooke, M. P., Jr.; Jaw, J.-Y. *J. Org. Chem.* **1986**, *51*, 758.

(8) Cooke, M. P., Jr. *Tetrahedron Lett.* **1979**, 2199.

(9) Three- through six-membered rings have been formed through metal–halogen exchange-initiated conjugated addition reactions: Cooke, M. P., Jr.; Widener, R. K. *J. Org. Chem.* **1987**, *52*, 1381.

(10) Cooke, M. P., Jr. *J. Org. Chem.* **1983**, *48*, 744.

(11) (a) Cooke, M. P., Jr.; Burman, D. L. *J. Org. Chem.* **1982**, *47*, 4955. (b) Cooke, M. P., Jr. *Ibid.* **1982**, *47*, 4963.

(12) Helmchen, G.; Wegner, G. *Tetrahedron Lett.* **1985**, *26*, 6047.

(13) While the configuration of the major isomers could not be firmly assigned from NMR spectra, they are believed to be isomers bearing halogen and methyl groups trans to COZ.

(14) (a) Olofson, R. A.; Hoskin, D. H.; Lotts, K. D. *Tetrahedron Lett.* **1978**, 1677. (b) Burford, C.; Cooke, F.; Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1977**, *99*, 4536.

(15) Reitter, B. E.; Sachdeva, Y. P.; Wolfe, J. F. *J. Org. Chem.* **1981**, *46*, 3945.

(16) MacDonald, T. L.; Narayanan, B. A.; O'Dell, D. E. *J. Org. Chem.* **1981**, *46*, 1504.

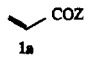
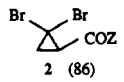
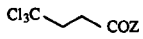
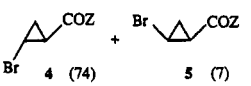
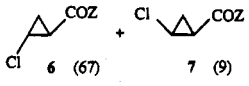
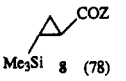
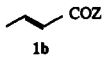
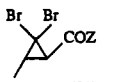
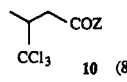
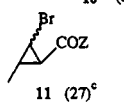
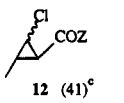
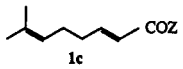
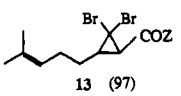
(17) Loupy, A.; LeFour, J. M.; Deschamps, B.; Seyden-Penne, J. *Nouv. J. Chim.* **1980**, *4*, 121.

(18) Cooke, M. P., Jr. *Tetrahedron Lett.* **1979**, 2199.

(19) (a) Bestmann, H. J.; Seng, F. *Angew Chem., Int. Ed. Engl.* **1962**, *1*, 116. (b) Grieco, P. A.; Finkelhor, R. S. *Tetrahedron Lett.* **1972**, 3781.

0022-3263/93/1958-0267$04.00/0

Table I. Reactions of Unsaturated Acylphosphoranes (1) with (Halomethyl)lithium Derivatives

entry	acceptor[a]	nucleophile	product (yield,[b] %)
1.	 1a	Br_3CLi	 2 (86)
2.		Cl_3CLi	 3 (90)
3.		Br_2CHLi	 4 (74) 5 (7)
4.		Cl_2CHLi	 6 (67) 7 (9)
5.		BrClCHLi	6 (72) 7 (7)
6.		$Me_3SiCHClLi$	 8 (78)
7.	 1b	Br_3CLi	 9 (91)
8.		Cl_3CLi	 10 (80)
9.		Br_2CHLi	 11 (27)[c]
10.		BrClCHLi	 12 (41)[c]
11.	 1c	Br_3CLi	 13 (97)

[a] Z = C(O)C(PPh_3)COOEt. [b] Isolated. [c] As an inseparable mixture of isomers.

of Hα (δ 3.86 in 4 owing to deshielding by the bromine atom compared with δ 3.3 in the cis isomer 5). A vicinal coupling constant J = 3.1 Hz between Hα and the adjacent methine hydrogen also supports this assignment insomuch as vicinal coupling constants for trans hydrogens in such systems are generally in the range of 3–5 Hz while in cis isomers J = 6–10 Hz.[20] The assignment is further supported by the steric compression-induced upfield C NMR shift of Cα in 5 (δ 25.4 vs 27.7 in 4).[21] Similarly, in cis isomer 7, Cα occurs at higher field than in trans isomer 6 (δ 26.3 vs 27.7), and the downfield shift of Hα in 6 (δ 3.8 vs δ 3.4 in 7) with J_{vic} = 3.0 Hz supports this assignment. While the J_{vic} = 6.2 Hz for Hα in 8 is not definitive, the strong (13%) NOE observed for Hα upon irradiation of the TMS group strongly suggests that 8 is the trans isomer. The vicinal coupling constant for Hα in 9 (8.6 Hz) is also larger than expected for the trans isomer, but a strong NOE (16%) on Hα upon methyl group irradiation make it likely that this compound possesses the trans structure shown. Compounds 11 and 12 were obtained as nonresolvable mixtures and their configurations could not be assigned; however, on the basis of the results above, it is likely that methyl and COZ groups enjoy a trans relationship and the mixtures are the result of the formations of epimers at the halocarbon center. A stereochemical assignment for 13 cannot be definitively made. The J_{vic} = 8.6 Hz suggests it to be the cis isomer, but it seems more likely that, as in the case of structurally similar 9 (with the same vicinal coupling constant) where NOE data more strongly supported the trans structure, this compound is also the trans isomer shown based on the precedents cited above.

Experimental Section

General Methods. For details, see the preface to the experimental section in ref 9. Solvent evaporation was accomplished with a rotary evaporator at water-pump pressures (15–20 mm). Extracts were dried over Na_2SO_4. Unsaturated acylphosphoranes **1a** and **1b** were prepared as previously described.[11b]

Ethyl 3-(2,2-Dibromocyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (2). A solution containing 402 mg (1.0 mmol) of **1a**[11b] and 430 μL (5.0 mmol) of bromoform in 13 mL of THF was stirred at −78 °C, and 0.72 mL (1.2 mmol) of 1.6 N *n*-BuLi was added dropwise. The mixture was stirred for 30 min and then treated with 15 mL of water and extracted with Et_2O. Concentration of the dried extract and purification by PTLC (7:10 hexane–EtOAc) give 497 mg (86%) of **2**: mp 138–139 °C (EtOAc–hexane); ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.77 (t, 3 H, J = 7.1 Hz), 1.72 (dd, 1 H, J = 7.0, 9.6 Hz), 2.17 (dd, 1 H, J = 7.1, 8.3 Hz), 3.90 (q, 2 H, J = 7.1 Hz), 3.86–4.01 (m, 1 H), 7.30–7.86 (m, 15 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 14.0, 25.7, 26.0, 38.3 (d, J = 9.4 Hz), 58.8, 72.6 (d, J = 111.4 Hz), 126.0 (d, J = 96.7 Hz), 128.5 (d, J = 12.1 Hz), 131.8 (d, J = 2.7 Hz), 133.3 (d, J = 9.4 Hz), 167.6 (d, J = 14.8 Hz), 186.1 (d, J = 5.4 Hz). Anal. Calcd for $C_{26}H_{23}Br_2O_3P$: C, 54.38; H, 4.04. Found: C, 54.24; H, 3.83.

Ethyl 6,6,6-Trichloro-3-oxo-2-(triphenylphosphoranylidene)hexanoate (3). Using the above procedure, 402 mg (1.0 mmol) of **1a**, 400 μL (5.0 mmol) of $CHCl_3$, and 0.78 mL (1.3 mmol) of 1.67 N *n*-BuLi gave, after PTLC (7:10 hexane–ethyl acetate), 470 mg (90%) of **3**: mp 124–125 °C (EtOAc–hexane); ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.67 (t, 3 H, J = 7.1 Hz), 2.0 (m, 2 H), 2.50 (m, 2 H), 3.76 (q, 2 H, J = 7.1 Hz), 7.3–7.8 (m, 15 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 13.7, 37.7 (d, J = 6.7 Hz), 50.5, 58.4, 70.7 (d, J = 110.1 Hz), 100.6, 126.5 (d, J = 94.0 Hz), 128.5 (d, J = 13.4 Hz), 131.6 (d, J = 2.7 Hz), 133.0 (d, J = 9.4 Hz), 167.7 (d, J = 14.8 Hz), 193.5 (d, J = 4.0 Hz). Anal. Calcd for $C_{26}H_{24}Cl_3O_3P$: C, 59.84; H, 4.64. Found: C, 59.86; H, 4.81.

General Procedure for Cyclopropanations with (Dihalomethyl)lithium Reagents. Ethyl 3-(2-Bromocyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (4, 5). A stirred solution containing 0.3 mL (1.5 mmol) of dicyclohexylamine in 4 mL of THF was treated with 1.5 mmol of *n*-BuLi at 0 °C.[24] After 10 min this solution was slowly added to a stirred solution containing 402 mg (1.0 mmol) of **1a** and 350 μL (3.0 mmol) of CH_2Br_2 in 10 mL of THF at −78 °C. After 30–40 min, the mixture was stirred at 20 °C for 15–30 min and then treated with 10 mL of water and twice extracted with Et_2O. The dried extracts gave after concentration and PTLC (4:1 CH_2Cl_2–EtOAc) 365 mg (74%) of **4** (higher R_f) and 32 mg (7%) of **5**. **4** (trans isomer): mp 118–119 °C (EtOAc–hexane); ^{1}H NMR (200 MHz) δ 0.68 (t, 3 H, J = 7.1 Hz), 1.24 (ddd, J = 9.4, 5.0, 4.5 Hz, 1 H), 1.46 (m, 1 H), 3.16 (ddd, J = 3.1, 4.4, 7.6 Hz, 1 H), 3.77 (q, 2 H, J = 7.1 Hz), 3.86 (ddd, J = 3.1, 6.0, 9.3 Hz, 1 H), 7.3–7.8 (m, 15 H); ^{13}C NMR (22.5 MHz) δ 13.7, 18.8, 21.8, 27.7 (d, J = 9.4 Hz), 58.5, 71.5 (d, J = 111.5 Hz), 126.5 (d, J = 92.7 Hz), 128.5 (d, J = 12.1 Hz), 131.6 (d, J = 4.0 Hz), 133.0 (d, J = 9.4 Hz), 167.8 (d, J = 14.8 Hz), 192.2 (d, J = 5.4 Hz). Anal. Calcd for $C_{20}H_{25}$-

(20) (a) Morris, D. G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; Part 1, p 101. (b) Barlet, R.; Vincens, M. *Tetrahedron* **1977**, *33*, 1291. (c) Dorsch, D.; Kunz, E. *Tetrahedron Lett.* **1985**, *26*, 3319. (d) Davies, H. M. L.; Hu, B. *J. Org. Chem.* **1992**, *57*, 3187.

(21) Martin, S. F.; Daniel, D.; Cherney, R. J.; Liras, S. *J. Org. Chem.* **1992**, *57*, 2523.

(22) Cooke, M. P., Jr.; Biciunas, K. P. *Synthesis* **1981**, 283.

(23) (a) Marbet, R.; Saucy, G. *Helv. Chim. Acta* **1967**, *50*, 2095. (b) Larock, R. C.; Oertle, K.; Potter, G. F. *J. Am. Chem. Soc.* **1980**, *102*, 190.

(24) Taguchi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 3010.

BrO_3P: C, 63.04; H, 4.88. Found: C, 63.05; H, 5.03. **5** (cis isomer): unstable solid; ^1H NMR (90 MHz) δ 0.66 (t, 3 H, J = 7.1 Hz), 1.26 (m, 1 H), 1.58 (q, 1 H, J = 6.0 Hz), 3.20–3.45 (m, 2 H), 3.74 (q, 2 H, J = 7.1 Hz), 7.30–7.85 (m, 15 H); ^{13}C NMR (22.5 MHz) δ 13.4, 13.8, 22.4, 25.4 (d, J = 9.4 Hz), 58.4, 72.3 (d, J = 110.1 Hz), 126.6 (d, J = 94.0 Hz), 128.5 (d, J = 12.1 Hz), 131.6 (d, J = 2.7 Hz), 133.4 (d, J = 9.4 Hz), 168.1 (d, J = 13.3 Hz), 189.4 (d, J = 5.4 Hz).

Ethyl 3-(2-Chlorocyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (6, 7). Using the procedure cited above for the preparation of **4** and **5**, 2 mmol of Chx_2NLi, 1 mmol of **1a**, and 3 mmol of CH_2Cl_2 gave, after PTLC (4:1 CH_2Cl_2–EtOAc) 301 mg (67%) of trans isomer **6** (higher R_f) and 42 mg (9%) of **7**. **6**: mp 138–139 °C (EtOAc–hexane); ^1H NMR (90 MHz) δ 0.68 (t, 3 H, J = 7.1 Hz), 1.05–1.50 (m, 2 H), 3.27 (m, 1 H), 3.77 (q, 2 H, J = 7.1 Hz), 3.7–4.0 (m, 1 H), 7.20–7.80 (m, 15 H); ^{13}C NMR (22.5 MHz) δ 13.7, 18.5, 27.7 (d, J = 9.4 Hz), 34.9, 58.5, 71.4 (d, J = 111.5 Hz), 126.5 (d, J = 94.0 Hz), 128.5 (d, J = 12.1 Hz), 131.1 (d, J = 2.7 Hz), 133.0 (d, J = 10.7 Hz), 167.8 (d, J = 14.8 Hz), 192.1 (d, J = 4.0 Hz). Anal. Calcd for $C_{20}H_{25}ClO_3P$: C, 69.26; H, 5.36. Found: C, 69.40; H, 5.20. **7**: mp 140–141 °C (EtOAc–hexane); ^1H NMR (200 MHz) δ 0.65 (t, 3 H, J = 7.1 Hz), 1.09 (m, 1 H), 1.56 (q, 1 H, J = 6.1 Hz), 3.41 (m, 2 H), 3.74 (q, 2 H, J = 7.1 Hz), 7.3–7.8 (m, 15 H); ^{13}C NMR (22.5 MHz) δ 13.1, 13.7, 26.3 (d, J = 9.4 Hz), 34.3, 58.3, 72.5 (d, J = 110.1 Hz), 126.6 (d, J = 94.0 Hz), 128.4 (d, J = 12.1 Hz), 131.1 (d, J = 2.7), 133.3 (d, J = 9.4 Hz), 168.0 (d, J = 14.8 Hz), 189.0 (d, J = 5.4 Hz). Anal. Calcd for $C_{20}H_{25}ClO_3P$: C, 69.26; H, 5.36. Found: C, 68.97; H, 5.47.

In a similar experiment using CH_2BrCl to generate BrClCHLi, **6** and **7** were obtained in yields of 72% and 7%, respectively.

Ethyl 3-(*trans*-2-(Trimethylsilyl)cyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (8). A solution containing 100 μL (0.7 mmol) of Me_3SiCH_2Cl and 110 μL (0.7 mmol) of TMEDA in 5 mL of THF was cooled to −78 °C and with stirring, treated with 1.0 mL (0.73 mmol) of 0.73 N *s*-BuLi.[14b] After 45 min, 200 mg (0.5 mmol) of **1a** in 2 mL of THF was added over 1 min. After 3 min, the dark yellow solution was allowed to warm to 20 °C over 5 min, and stirring was continued for 15 min. Water (100 μL) was added, and after solvent removal the residue was purified by PTLC (17:1 CH_2Cl_2–EtOAc), giving 192 mg (78%) of **8** as an oil: ^1H NMR (500 MHz) δ −0.04 (s, 9 H), 0.21 (m, 1 H, J = 8.1, 6.2, 10.4 Hz), 0.59 (m, 1 H, J = 8.1, 7.5, 2.4 Hz), 0.67 (t, 3 H, J = 7.1 Hz), 0.99 (ddd, 1 H, J = 10.4, 4.4, 2.4 Hz), 3.24 (ddd, 1 H, J = 7.5, 6.2, 4.4 Hz), 3.74 (m, 2 H), 7.35–7.70 (m, 15 H); ^{13}C NMR (22.5 MHz) δ −2.3, 9.4, 12.4, 13.9, 20.9 (d, J = 9.4 Hz), 58.3, 71.0 (d, J = 112.8 Hz), 127.3 (d, J = 94.0 Hz), 128.3 (d, J = 13.4 Hz), 131.3 (d, J = 2.7 Hz), 133.0 (d, J = 9.4 Hz), 167.9 (d, J = 14.7 Hz), 196.6 (d, J = 4.0 Hz).

Ethyl 3-(2,2-Dibromo-*trans*-3-methylcyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (9). In the manner described above for the preparation of **2**, 208 mg (0.5 mmol) of **16**, 220 μL of $HCBr_3$, and 0.75 mmol of *n*-BuLi gave, after 60 min at −78 °C, 269 mg (91%) of **9**: mp 161–162 °C (EtOAc–hexane); ^1H NMR (90 MHz) δ 0.74 (t, 3 H, J = 7.1 Hz), 1.25 (d, 3 H, J = 6.3 Hz), 2.1 (m, 1 H), 3.45 (d, 1 H, J = 8.5 Hz), 3.86 (q, 2 H, J = 7.1 Hz), 7.30–7.86 (m, 15 H); ^{13}C NMR (22.5 MHz) δ 13.9, 16.4, 28.6, 35.9, 44.3 (d, J = 9.4 Hz), 58.8, 72.5 (d, J = 110.1 Hz), 126.4 (d, J = 106.1 Hz), 128.4 (d, J = 13.4 Hz), 131.7 (d, J = 2.7 Hz), 133.2 (d, J = 10.6 Hz), 167.7 (d, J = 14.8 Hz), 186.8 (d, J = 5.4 Hz). Anal. Calcd for $C_{27}H_{25}Br_2O_3P$: C, 55.13; H, 4.28. Found: C, 54.90; H, 4.43.

Ethyl 5-(Trichloromethyl)-3-oxo-2-(triphenylphosphoranylidene)hexanoate (10). As described in the preparation of **3**, 208 mg (0.5 mmol) of **16**, 200 μL (2.5 mmol) of $CHCl_3$, and 1.0 mmol of *n*-BuLi gave, after 40 min at −78 °C, 214 mg (80%) of **10**: mp 163–165 °C (EtOAc–hexane); ^1H NMR (90 MHz) δ 0.68 (t, 3 H, J = 7.1 Hz), 1.22 (d, 3 H, J = 7.1 Hz), 3.22 (m, 1 H), 3.40 (d, 2 H, J = 7.2 Hz), 3.76 (q, 2 H, J = 7.1 Hz), 7.30–7.86 (m, 15 H); ^{13}C NMR (22.5 MHz) δ 13.7, 17.1, 43.7 (d, J = 8.1 Hz), 51.1, 58.5, 71.7 (d, J = 110.1 Hz), 106.7, 126.7 (d, J = 94.3 Hz), 128.5 (d, J = 12.1 Hz), 131.6 (d, J = 2.7 Hz), 133.0 (d, J = 9.4 Hz), 167.7 (d, J = 14.8 Hz), 192.5 (d, J = 4.0 Hz). Anal. Calcd for $C_{27}H_{26}Cl_3O_3P$: C, 60.52; H, 4.89. Found: C, 60.60; H, 4.87.

Ethyl 3-(2-Bromo-3-methylcyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (11). In a manner similar to that described for the preparation of **4**, 208 mg (0.5 mmol) of **16**, 220 μL (2.5 mmol) of CH_2Br_2, and 1.0 mmol of lithium diisopropylamide (LDA) gave, after 50 min at −78 °C and 15 min at 20 °C, 27 mg (27%) of **11** as an oily nonseparable mixture of isomers: ^1H NMR (90 MHz) δ 0.69 (t, 3 H, J = 7.1 Hz), 1.33 (b, 4 H), 3.45 (m, 2 H), 3.77 (q, 2 H, J = 7.1 Hz), 4.30–7.85 (m, 15 H); ^{13}C NMR (22.5 MHz, major isomer) δ 13.8, 15.1, 21.8, 35.3 (d, J = 9.4 Hz), 58.5, 72.0 (d, J = 110.5 Hz), 126.7 (d, J = 94.0 Hz), 128.5 (d, J = 13.4 Hz), 131.6 (d, J = 2.7 Hz), 133.0 (d, J = 9.4 Hz), 168.0 (d, J = 14.8 Hz), 193.0 (d, J = 4.0 Hz).

Ethyl 3-(2-Chloro-3-methylcyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (12). In the manner described for the preparation of **11**, 208 mg (0.5 mmol) of **1b**, 100 μL (1.5 mmol) of CH_2BrCl, and 1.5 mmol of LDA gave, after 25 min at −78 °C and 60 min at 20 °C, 96 mg (41%) of **12** as a thick oil: ^1H NMR (90 MHz) δ 0.68 (t, 3 H, J = 7.1), 0.95–1.60 (m, 1 H), 1.30 (d, 3 H, J = 7.0 Hz), 3.4 (m, 2 H), 3.77 (q, 2 H, J = 7.1 Hz), 7.30–7.85 (m, 15 H); ^{13}C NMR (22.5 MHz, major isomer) δ 12.7, 13.8, 22.2, 35.2 (d, J = 9.4 Hz), 41.7, 58.5, 71.7 (d, J = 110.1 Hz), 126.7 (d, J = 92.7 Hz), 128.5 (d, J = 13.4 Hz), 131.6 (d, J = 2.7 Hz), 133.0 (d, J = 9.4 Hz), 168.0 (d, J = 14.8 Hz), 192.5 (d, J = 4.0 Hz).

Ethyl 9-Methyl-3-oxo-2-(triphenylphosphoranylidene)-4,8-decadienoate (1c). To a stirred suspension of 80 mg (3.3 mmol) of NaH in 15 mL of THF was added 1.56 g (3 mmol) of diethyl 2,4-dioxo-4-ethoxy-3-(triphenylphosphoranylidene)-butanephosphonate.[22] After 35 min, a solution containing 1.02 g (9.1 mmol) of 5-methyl-4-hexenal[23] in 6 mL of THF was added. After 40 min, the mixture was treated with water and twice extracted with ether. Concentration of the dried extracts gave, after column chromatography (SiO_2, CH_2Cl_2–EtOAc), 583 mg of **1c** as an oil: ^1H NMR (90 MHz) δ 0.67 (t, 3 H, J = 7.1 Hz), 1.57 (s, 3 H), 1.65 (s, 3 H), 2.17 (b, 4 H), 3.75 (q, 2 H, J = 7.1 Hz), 5.11 (b, 1 H), 6.67 (m, 1 H), 7.30–7.86 (m, 16 H).

Ethyl 3-(2,2-Dibromo-3-(4-methyl-3-penten-1-yl)cyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (13). In the manner described for the preparation of **2**, 145.3 mg (0.3 mmol) of **1c**, 130 μL (1.5 mmol) of $CHBr_3$, and 0.3 mmol of *n*-BuLi was stirred at −78 °C for 45 min where upon an additional 0.3 mmol of *n*-BuLi was added. After 25 min the mixture was quenched with 15 mL of water and extracted with Et_2O. Chromatography (SiO_2, 4:1:1 hexane–CH_2Cl_2–EtOAc) gave 191 mg (97%) of **13** as a yellow oil: ^1H NMR (90 MHz) δ 0.74 (t, 3 H, J = 7.1 Hz), 1.54 (s, 3 H), 1.62 (s, 3 H), 1.3–1.7 (b, 2 H), 1.95–2.25 (m, 2 H), 3.54 (d, 1 H, J = 8.6 Hz), 3.87 (q, 2 H, J = 7.1 Hz), 5.11 (b, 1 H), 7.30–7.86 (m, 15 H); ^{13}C NMR (22.5 MHz) δ 13.9, 17.6, 25.7, 26.6, 32.1, 33.7, 35.1, 43.3 (d, J = 9.4 Hz), 58.8, 72.5 (d, J = 110.1 Hz), 123.5, 132.1, 126.4 (d, J = 103.4 Hz), 128.5 (d, J = 12.1 Hz), 131.7 (d, J = 2.7 Hz), 133.3 (d, J = 10.7 Hz), 167.7 (d, J = 14.8 Hz), 186.8 (d, J = 5.4 Hz).

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Supplementary Material Available: ^1H NMR spectra of **1c**, **5**, **8**, **11**, **12**, and **13** (6 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.