centrated under vacuum. The residue was purified by flash chromatography on silica gel using a step gradient of methanol in methylene chloride as eluant. The appropriate product fractions were combined and concentrated to a gum. Crystallization by diffusion of diethyl ether into a methylene chloride solution of this gum gave 2.12 g (3.4 mmol 85%) of **7a**: UV_{max} (CH_3OH) 279 nm; UV_{min} 238 nm.

To a 250 mg portion of **7a** dissolved in 1 mL of methylene chloride was added 20 mL of 2% trichloroacetic acid in methylene chloride. After 40 min. the reaction was poured into 20 mL of 2% $NaHCO_3$ and then extracted with two 20-mL portions of methylene chloride. The combined organic layers were concentrated under vacuum. The residue was purified by flash chromatography on silica gel, using a step gradient of methanol in methylene chloride as eluant. The appropriate product fractions were combined and concentration to a gum. Crystallization by diffusion of diethyl ether into a methylene chloride solution of this gum gave 85 mg (69%) of **7b**: UV_{max} (CH_3OH) 279 nm (ϵ 23.1×10^3); UV_{min} 238 nm (ϵ 3.7×10^3); mp 209-211 °C. Anal. Calcd for $C_{14}H_{17}N_5O_4$: C, 52.63; H, 5.38; N, 21.94. Found: C, 52.41; H, 5.19; N, 21.63.

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Registry No. **1a**, 68892-42-2; **1b**, 68892-41-1; **4a**, 82921-57-1; **4b**, 90678-72-1; **7a**, 100205-38-7; **7b**, 100190-48-5; 2-(4-nitrophenyl)ethanol, 100-27-6.

Cyclopropane Derivatives through Charge-Directed Conjugate Addition Reactions of Unsaturated Acylphosphoranes

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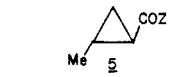
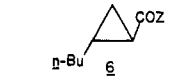
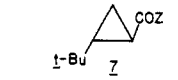
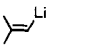
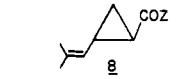
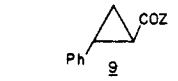
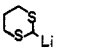
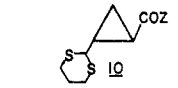
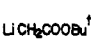
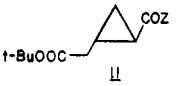
There has been considerable interest over the years in the construction of cyclopropane derivatives through Michael-initiated intramolecular alkylation reactions of γ-halo Michael acceptors. Allylic substitution and 1,2-addition processes are often competing, if not dominant, side reactions. Certain doubly activated alkylidenemalonate derivatives bearing a γ-leaving group give cyclopropyl derivatives in good yields when treated with nucleophiles such as cyanide,[1] methoxide,[1] thiolate,[1c] and borohydride.[1c]

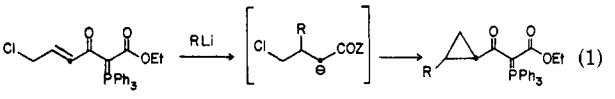
The singly activated 4-halocrotonate system also undergoes such reactions but only with certain stabilized nucleophiles such as lithium thiolates,[2] certain sulfur-based carbanions,[3] and the enolates of some esters.[4] More powerful nucleophiles generally are not successfully employed. Methyl 4-bromocrotonate and phenylmagnesium bromide give, after saponification of the reaction mixture, *trans*-2-phenylcyclopropanecarboxylic acid in only 13% yield.[5] Michael acceptors with the structural features necessary for cyclopropane formation (good γ-leaving groups) generally undergo reduction reactions with organocopper reagents.[6]

Table I. Reaction of 1 with Nucleophiles

RLi	Product[a]	Yield(%)[b]
MeLi		91
n-BuLi		91
t-BuLi		77
		67
PhLi		84
		76
		91

[a] COZ = C(O)C(Ph_3P)COOEt. [b] Isolated.

We have previously shown that unsaturated acylphosphoranes undergo charge-directed conjugate addition reactions with a wide range of nucleophiles[7] and that such reactions may be used to initiate intramolecular cyclization reactions leading to five- and six-membered rings.[8] We now report that chlorinated acceptor 1 reacts with a variety of nucleophiles heretofore not successfully employed in addition-initiated cyclopropanation reactions giving cyclopropane derivatives[3] as shown in eq 1. When coupled

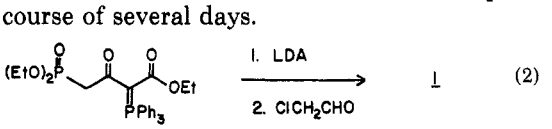


(1)

1 2 3

with the functional group transformations previously developed for such acylphosphoranes, a variety of cyclopropyl carboxyl[9] and ketone[10] derivatives become available by this process.

Acceptor 1 is readily prepared by Emmons-Wadsworth-Horner condensation of anhydrous chloroacetaldehyde[11] with the lithium salt of phosphonate 4 (eq 2).[12] Crystalline 1 is stable for months but solutions decompose over the course of several days.



(2)

4

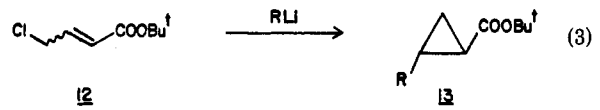
Treatment of 1 with a variety of organolithium reagents in THF results in the formation of cyclopropyl derivatives

(1) (a) DeVos, M. J.; Krief, A. *Tetrahedron Lett.* **1979**, 1891. (b) Kolsaker, B. P.; Storesund, H. J. *J. Chem. Soc., Chem. Commun.* **1972**, 375. (c) Verhe, R.; DeKimpe, N.; DeBuyck, L.; Courtheyn, C.; Schamp, N. *Bull. Soc. Chim. Belg.* **1977**, *86*, 55.
(2) Little, R. D.; Dawson, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 4607.
(3) Ghera, E.; Ben-David, Y. *Tetrahedron Lett.* **1979**, 4603.
(4) (a) Prempree, P.; Radviroongit, S.; Thebtaranonth, Y. *J. Org. Chem.* **1983**, *48*, 3553. (b) Yamaguchi, M.; Tsukamoto, M.; Hirao, I. *Tetrahedron Lett.* **1985**, *26*, 1723.
(5) Ratney, R.; English, J., Jr. *J. Org. Chem.* **1960**, *25*, 2213.
(6) Posner, G. H. *Org. React. (N.Y.)* **1971**, *19*, 1.
(7) Cooke, M. P., Jr.; Goswami, R. *J. Am. Chem. Soc.* **1977**, *99*, 642.
(8) Cooke, M. P., Jr. *Tetrahedron Lett.* **1979**, 2199.
(9) Cooke, M. P., Jr. *J. Org. Chem.* **1983**, *48*, 744.
(10) (a) Cooke, M. P., Jr.; Burman, D. L. *J. Org. Chem.* **1982**, *47*, 4955. (b) Cooke, M. P., Jr. *Ibid.* **1982**, *47*, 4963.
(11) Gross, H. *J. Prakt. Chem.* **1963**, *21*, 99.
(12) Cooke, M. P., Jr.; Biciunas, K. P. *Synthesis* **1981**, 283.

0022-3263/86/1951-0758$01.50/0

in good to excellent yields as shown in Table I. The reaction is not limited to the use of only highly reactive lithium reagents as seen in the successfully preparation of **10** and **11** from 2-lithiodithane and the enolate of *tert*-butyl acetate, respectively. Only the trans stereoisomer is observed in each case—stereochemistry being assigned on the basis of precedent[2,4a,8] and on a direct determination in one case. Oxidation of **9** with NaOCl[9] gave *trans*-2-phenylcyclopropanecarboxylic acid in 78% yield.

In light of our earlier finding that *tert*-butyl esters of α,β-unsaturated acids can give a substantial amount of 1,4-addition product when treated with alkyllithium reagents,[13] we have also briefly examined the reactions of *tert*-butyl 4-chlorocrotonate (**12**) with reactive lithium reagents (eq 3). Treatment of the **12E** with *n*-BuLi in



12 **13** (3)

THF at −78 °C gave a complex mixture containing **13** (R = *n*-Bu) in 34% yield.[14] Trans stereochemistry is assigned on the basis of the identity of this product with that obtained from the cyclopropanation of *tert*-butyl (*E*)-2-heptenoate with dimethyloxosulfonium methylide—a reaction known to give trans products.[15] Isobutenyllithium and **12E** gave **13** (R = $(CH_3)_2C{=}CH$) in 52% isolated yield.

Interestingly, phenyllithium and **12E** gave **13** (R = Ph)[16] in 64% yield while **12Z** gave none of this product under similar conditions. This observation may support the transition-state model proposed by Little[2] in which the Michael addition step occurs through a cyclic transition state involving oxygen coordination with lithium in the *S*-cis conformer of the acceptor. The failure observed with **12Z** may be due to its inability to readily adopt the *S*-cis conformation.

In summary, ylide **1** appears to be the most versatile acceptor for Michael-initiated cyclopropanation yet reported.

Experimental Section

NMR spectra were recorded at 90 MHz with a JEOL FX-90q spectrometer or at 200 MHz with a Nicolet NT-200 spectrometer as indicated. Chemical shifts are reported in parts per million (δ) relative to added tetramethylsilane. Preparative thick-layer chromatography (PTLC) was performed on 20 × 20 cm plates coated with a 1–2-mm layer of Merck silica gel 60 PF-254. Baker 60–200 mesh silica powder was used for column chromatography. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points and boiling points are uncorrected. Bulb-to-bulb distillations of the Kugelrohr type were conducted at the air oven temperatures and pressures cited.

Methyllithium in diethyl ether, *n*-butyllithium in hexane, *tert*-butyllithium in pentane, and phenyllithium in cyclohexane–diethyl ether were obtained from Aldrich Chemical Co. and titrated[17] prior to use. All reactions involving air-sensitive materials were conducted under an argon atmosphere. Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl prior to use.

Ethyl 6-Chloro-3-oxo-2-(triphenylphosphoranylidene)-(*E*)-4-hexenoate (1). To a stirred solution of lithium diisopropylamide (LDA) prepared from 170 μL of diisopropylamine and 1.2 mmol of *n*-BuLi in 6 mL of THF was slowly added 527 mg (1.0 mmol) of **4**[12] in 5 mL of THF at −78 °C. The mixture was kept at 78 °C for 10 min, stirred at 20 °C for 10 min, and then recooled to −78 °C. A solution containing 138 mg (1.76 mmol) of freshly distilled anhydrous chloroacetaldehyde[11] in 3 mL of THF was slowly added. After being stirred at −78 °C for 15 min, the mixture was stirred at 20 °C for 20 min and then quenched by the addition of water (15 mL). The mixture was extracted with ether (2 × 20 mL), and the extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (1:1 hexane–ether), giving 322 mg (72%) of **1**, which solidified after the solvent was removed under reduced pressure. Solutions of **1** are found to be unstable over several days—especially when heated to greater than 25 °C. Concentrated solutions of **1** from the chromatographic process slowly deposited crystals of **1** which are quite stable: mp 114–115 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.66 (t, 3 H, J = 7.1 Hz), 3.73 (q, 2 H, J = 7.1 Hz), 4.17 (dd, 2 H, J = 6.7, 1.3 Hz), 6.60 (dt, 1 H, J = 6.7, 17.1 Hz), 7.32–7.82 (m, 16 H). Anal. Calcd for $C_{27}H_{24}ClO_3P$: C, 69.26; H, 5.37. Found: C, 69.40; H, 5.47.

Ethyl 3-(*trans*-2-Methylcyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (5). A solution containing 135 mg (0.3 mmol) of **1** in 3 mL of THF was cooled to −78 °C, and with stirring there was added 0.19 mL (0.3 mmol) of 1.6 M MeLi. After 15 min at −78 °C, the mixture was quenched by the addition of several drops of water, and the solvent was removed under reduced pressure. The residue was purified by PTLC (1:4:1 EtOAc–CH_2Cl_2–hexane), giving 117 mg (91%) of **5**: mp 114 °C (from EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.51 (m, 1 H), 0.65 (t, 3 H, J = 7.1 Hz), 1.05 (m, 1 H), 1.12 (d, 3 H, J = 5.6 Hz), 1.25 (m, 1 H), 3.13 (m, 1 H), 3.74 (q, 2 H, J = 7.1 Hz), 7.3–7.8 (m, 15 H). Anal. Calcd for $C_{27}H_{27}O_3P$: C, 75.33; H, 6.32. Found: C, 75.03; H, 6.08.

Ethyl 3-(*trans*-2-Butylcyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (6). In accordance with the above procedure for the preparation of **5**, 135 mg (0.3 mmol) of **1** and 0.39 mL (0.31 mmol) of 0.81 M *n*-BuLi in hexane gave 129 mg (91%) of pure **6** after silica gel chromatography (5:1 hexane–EtOHc): mp 116–117 °C (from EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.66 (t, 3 H, J = 7.1 Hz), 0.51–1.40 (br, 12 H), 3.19 (m, 1 H), 3.75 (q, 2 H, J = 7.1 Hz), 7.28–7.78 (m, 15 H). Anal. Calcd for $C_{30}H_{33}O_3P$: C, 76.25; H, 7.04. Found: C, 76.34; H, 7.11.

Ethyl 3-(*trans*-2-*tert*-Butylcyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (7). In the manner described above, 135 mg (0.3 mmol) of **1** and 0.4 mL (0.33 mmol) of 0.82 M *t*-BuLi in pentane gave after chromatography on silica gel (1:3 EtOAc–hexane) 108 mg (76%) of **7** as an oil: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.70 (t, 3 H, J = 7 Hz), 0.91 (s, 9 H), 0.51–1.24 (m, 3 H), 3.35 (m, 1 H), 3.77 (q, 2 H, J = 7 Hz), 7.3–7.8 (m, 15 H).

Ethyl 3-(*trans*-2-Isobutenylcyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (8). To a stirred solution containing 3.0 mmol of isobutenyllithium[18] in 10 mL of dry ether was added at −78 °C 451 mg (1.0 mmol) of **1** in 5 mL of THF. After 10 min at −78 °C 15 mL of water was added, and the mixture was extracted with ether (2 × 30 mL). The extracts were dried over Na_2SO_4 and concentrated, and the residue was chromatographed on silica gel (1:4 EtOHc–hexane), giving 315 mg (67%) of **8**: mp 150–151 °C (from EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.65 (t, 3 H, J = 7 Hz), 0.75 (m, 1 H), 1.25 (m, 1 H), 1.69 (s, 6 H), 1.90 (m, 1 H), 3.40 (m, 1 H), 3.74 (q, 2 H, J = 7 Hz), 4.76 (d, 1 H, J = 9 Hz), 7.3–7.8 (m, 15 H). Anal. Calcd for $C_{30}H_{31}O_3P$: C, 76.58; H, 6.64. Found: C, 76.25; H, 6.67.

Ethyl 3-(*trans*-2-Phenylcyclopropyl)-3-oxo-2-(triphenylphosphoranylidene)propanoate (9). In the manner described for the preparation of **5**, 135 mg (0.3 mmol) of **1** and 0.13 mL (0.31 mmol) of 2.4 M PhLi in cyclohexane–ether gave, after chromatography on silica gel (5:1 hexane–EtOAc), 125 mg (84%) of **9**: mp 125–126 °C (from EtOAc–hexane); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.62 (t, 3 H, J = 7 Hz), 1.14 (m, 1 H), 1.48 (m, 1 H), 2.35 (m, 1 H), 3.83 (m, 1 H), 3.72 (q, 2 H, J = 7 Hz), 7.1–7.3 (m, 5 H), 7.3–7.8 (m, 15 H). Anal. Calcd for $C_{32}H_{29}O_3P$: C, 78.03; H, 5.93. Found: C, 77.86; H, 6.08.

(13) Cooke, M. P., Jr. *J. Org. Chem.* **1984**, *49*, 1144.
(14) The yield was determined by GC using an added internal standard.
(15) (a) Kaiser, C.; Trost, B. M.; Beeson, J.; Weinstock, J. *J. Org. Chem.* **1965**, *30*, 3972. (b) Landor, S. R.; Punja, N. *J. Chem. Soc. C* **1967**, 2495.
(16) Stereochemistry was shown to be trans by conversion to *trans*-2-phenylcyclopropanecarboxylic acid (*p*-TsOH·H_2O in PhH, 70 °C, 5 h).
(17) Watson, S. C.; Eastham, J. F. *J. Org. Chem.* **1967**, *9*, 165.
(18) (a) Gadwook, R. C.; Lett, R. M. *J. Org. Chem.* **1982**, *47*, 2268. (b) Braude, E. A.; Timmons, C. J. *J. Chem. Soc.* **1950**, 2000.

Oxidation[9] of **9** was performed by the slow addition of a solution containing 2.9 mL (2.3 mmol) of 0.8 N NaOCl (Chlorox) and 0.8 mL of 2 N NaOH to 418 mg (0.85 mmol) of **9** in 12 mL of acetonitrile followed by stirring for 2.5 h at 20 °C. The mixture was saturated with $NaHSO_3$ and evaporated to dryness under reduced pressure. The residue was dissolved in 5 mL of water and brought to pH 10 with 2 N NaOH, extracted with ether, acidified with concentrated HCl, and again extracted with ether. Solvent removal from the dried extracts gave 107 mg (78%) of *trans*-2-phenylcyclopropanecarboxylic acid: mp 93 °C (from water) (lit.[19] mp 93 °C).

Ethyl 3-[*trans*-2-(1,3-Dithianyl)cyclopropyl]-3-oxo-2-(triphenylphosphoranylidene)propanoate (10). A solution of 2-lithio-1,3-dithiane[20] (0.36 mmol) was prepared by adding 0.3 mL of 1.24 M *n*-BuLi to 43 mg of 1,3-dithiane in 3 mL of THF at −20 °C followed by stirring at −20 °C for 1.5 h. To this solution was added 135 mg (0.3 mmol) of **1** in 3 mL of THF. After 10 min the mixture was brought to 25 °C and stirred for 15 min and then treated with 6 mL of water. The mixture was extracted with ether (2 × 20 mL), and the extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue on 12 g of silica (1:3 EtOAc–hexane) gave 126 mg of **10**: mp 70–71 °C (from EtOHc–hexane); ^1H NMR ($CDCl_3$) δ 0.8–1.3 (m, 2 H), 1.4–2.3 (m, 1 H), 2.02 (m, 2 H), 2.81 (m, 4 H), 3.5–3.9 (m, 4 H), 7.3–7.8 (m, 15 H). Anal. Calcd for $C_{30}H_{31}O_3PS_2$: C, 67.39; H, 5.84. Found: C, 67.45; H, 6.10.

Ethyl 3-[*trans*-2-((*tert*-butoxycarbonyl)methyl)cyclopropyl]-3-oxo-2-(triphenylphosphoranylidene)propanoate (11). A solution of *tert*-butyl lithioacetate[21] (0.36 mmol) was prepared by adding 49 μL of *tert*-butyl acetate to a solution containing 0.36 mmol of LDA in 3 mL of THF at −20 °C. After 10 min, a solution containing 135 mg (0.3 mmol) of **1** in 3 mL of THF was added with continued stirring for 20 min. The mixture was treated with 6 mL of water and extracted with ether (2 × 20 mL), and the extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue on 12 g of silica (1:3 EtOAc–hexane) gave 145 mg (91%) of **11** as a pale yellow oil: ^1H NMR ($CDCl_3$, 90 MHz) δ 0.65 (t, 3 H, J = 7 Hz), 1.43 (s, 9 H), 0.7–1.6 (m, 3 H), 2.25 (m, 2 H), 3.23 (m, 1 H), 3.73 (q, 2 H, J = 7 Hz), 7.3–7.8 (m, 15 Hz).

***tert*-Butyl 4-Chloro-2-butenoate (12).**[22] To a solution containing 19.4 g (0.052 mol) of *tert*-butyl (triphenylphosphoranylidene)acetate[10a] in 60 mL of CH_2Cl_2 was added over 1 h at 25 °C a solution containing 4.53 g (0.058 mol) of freshly distilled anhydrous chloroacetaldehyde[11] in 40 mL of CH_2Cl_2. After an additional 40 min the mixture was heated under reflux for 2 h. Solvent was removed under reduced pressure, and the residue was triturated with 250 mL of pentane. After standing overnight, triphenylphosphine oxide was removed by filtration, and the filtrate was concentrated under reduced pressure. Chromatography on 250 g of silica gave, upon elution with 5:1 petroleum ether–CH_2Cl_2, 1.4 g (16%) of **12Z** followed by 6.4 g (70%) of **12E**. **12Z**: bp 69–70 °C (4.5 mm); ^1H NMR ($CDCl_3$, 90 MHz) δ 1.49 (s, 9 H), 4.63 (dd, 2 H, J = 6.8, 1.5 Hz), 5.76 (dt, 1 H, J = 11.5, 1.5 Hz), 6.22 (dt, 1 H, J = 11.5, 6.8 Hz). Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.42. Found: C, 54.80; H, 7.85. **12E**: bp 95–97 °C (15 mm); ^1H NMR ($CDCl_3$, 90 MHz) δ 1.49 (s, 9 H), 4.14 (dd, 2 H, J = 6.1, 1.7 Hz), 6.01 (td, 1 H, J = 15.4, 1.7 Hz), 6.87 (td, 1 H, J = 15.4, 6.1 Hz). Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.42. Found: C, 54.22; H, 7.34.

***tert*-Butyl *trans*-2-Butylcyclopropanecarboxylate (13, R = *n*-Bu).** To a solution containing 271 mg (1.53 mmol) of **12E** in 5 mL of THF at 78 °C was slowly added 1.06 mL (1.7 mmol) of 1.6 M *n*-BuLi in hexane. After 20 min water was added along with 100 μL of undecane (GC standard). GC analysis showed the presence of **13** (R = Bu) in 34% yield. The mixture was treated with 10 mL of water and extracted with ether (2 × 15 mL). The dried extracts ($MgSO_4$) gave after concentration and chromatography on 15 g of silica (4:1 petroleum ether–CH_2Cl_2) 66 mg (22%) of **13** (R = Bu). An analytical sample was obtained by bulb-to-bulb distillation (130 °C, 0.5 mm): ^1H NMR ($CDCl_3$, 90 MHz) δ 1.44 (s, 9 H), 0.5–2.0 (m, 13 H). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.84; H, 11.11.

***tert*-Butyl *trans*-2-Isobutenylcyclopropanecarboxylate (13, R = $(CH_3)_2C{=}CH$).** To a solution of 9.3 g (69 mmol) of isobutenyl bromide in 100 mL of ether at −78 °C was added dropwise over 20 min 84 mL (69 mmol) of 0.82 M *t*-BuLi in pentane. The mixture was stirred for 10 min at −78 °C and for 20 min at 0 °C and then recooled to −78 °C, whereupon a solution containing 4.21 g (24 mmol) of **12E** in 25 mL of THF was added over 3 min. After 20 min the mixture was warmed to 20 °C, stirred for 20 min and then treated with 30 mL of water. The mixture was extracted with ether (3 × 50 mL), and the extracts were washed with brine and dried over Na_2SO_4. Removal of solvent under reduced pressure gave an oil, which upon chromatography on 150 g silica (3:1 petroleum ether–CH_2Cl_2) gave 2.29 g (51%) of **13** (R = $(CH_3)_2C{=}CH$). An analytical sample was obtained by bulb-to-bulb distillation [130 °C (1 mm)]: ^1H NMR ($CDCl_3$, 90 MHz) δ 0.66–1.55 (m, 3 H), 1.45 (s, 9 H), 1.68 (br s, 3 H), 1.74 (br s, 3 H), 2.0 (m, 1 H), 4.60 (d, 1 H, J = 8.5 Hz). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.48; H, 10.34.

***tert*-Butyl *trans*-2-Phenylcyclopropanecarboxylate (13, R = Ph).** A solution of 177 mg (1.0 mmol) of **12E** in 4 mL of THF was cooled to −78 °C and treated dropwise with 0.82 mL (1.1 mmol) of 1.35 M PhLi in cyclohexane–ether. After 20 min, the mixture was brought to 25 °C, stirred for 10 min, and then treated with 5 mL of wet ether. GC analysis with the aid of 100 μL of added pentadecane indicated the presence of **13** in 64% yield. Concentration of the mixture followed by chromatography of the residue on 15 g of silica (petroleum ether followed by 3:1 petroleum ether–CH_2Cl_2) and bulb-to-bulb distillation [135 °C (0.02 mm)] gave 121 mg (56%) of **13** (R = Ph) as an oil:[16] ^1H NMR ($CDCl_3$, 90 MHz) δ 1.1–1.6 (m, 2 H), 1.46 (s, 9 H), 1.80 (m, 1 H), 2.40 (m, 1 H), 7.15 (m, 5 H). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.93; H, 8.40.

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Registry No. **1**, 100207-37-2; **4**, 78980-76-4; **5**, 100207-38-3; **6**, 100207-39-4; **7**, 100207-40-7; **8**, 100207-41-8; **9**, 100229-26-3; **10**, 100207-42-9; **11**, 100207-43-0; **12E**, 56905-09-0; **12Z**, 56904-91-7; **13** (R = Ph), 5279-78-7; **13** (R = *n*-Bu), 100207-44-1; **13** (R = $(CH_3)_2C{=}CH$), 100207-45-2; *tert*-butyl (triphenylphosphoranylidene)acetate, 35000-38-5; chloroacetaldehyde, 107-20-0; *trans*-2-phenylcyclopropanecarboxylic acid, 939-90-2; isobutenyl bromide, 3017-69-4.

(19) Burger, A.; Yost, W. L. *J. Am. Chem. Soc.* **1948**, *70*, 2198.
(20) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1075.
(21) Brockson, T. J.; Petragnani, N.; Rodrignes, R.; Lascala, H. *Synthesis* **1975**, 396.
(22) Stotter, P. L.; Hill, K. A. *Tetrahedron Lett.* **1975**, 1679.

Synthesis of the Aggregation Pheromone of the Square-Necked Grain Beetle *Cathartus quadricollis*

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The square-necked grain beetle (*Cathartus quadricollis* (Guêr.)) is one of the most common beetles found in stored corn in the southern United States.[1] In cornfields, it is almost always found on damaged or exposed ears. This beetle resembles, in morphology and habit, other grain-infesting beetles in the genera *Cryptolestes*[2–5] and *Ory-*

(1) "Stored Grain Pests", United States Department of Agriculture, Farmers' Bulletin No. 1260, p 21.
(2) Borden, J. H.; Dolinski, M. G.; Chong, L.; Verigin, V.; Pierce, H. D., Jr.; Oehlschlager, A. C. *Can. Entom.* **1979**, *111*, 581.
(3) Wong, J. W.; Verigin, V.; Oehlschlager, A. C.; Borden, J. H.; Pierce, H. D., Jr.; Pierce, A. M.; Chong, L. *J. Chem. Ecol.* **1983**, *9*, 451.
(4) Oehlschlager, A. C.; Wong, J. W.; Verigin, V. G.; Pierce, H. D., Jr. *J. Org. Chem.* **1983**, *48*, 5009.

0022-3263/86/1951-0760$01.50/0