generated using the direct method program MULTAN.[5] All nonhydrogen atoms were located on the first E map. Full matrix least-squares refinement of positional and isotropic thermal parameters of nonhydrogen atoms reduced R to 0.184. Anisotropic refinement brought R down to 0.065. A difference map at this stage revealed all the hydrogens and two more cycles of refinement (anisotropic for nonhydrogens and isotropic for hydrogens) brought R down to the final value of 0.053. The refinement was based on F_0, the quantity minimized being $\Sigma w(F_o - F_c)^2$. The scattering factors used were those of Hanson et al.[6] No correction was applied for extinction.

Voleneol Monoacetate. Hydrolysis of voleneol diacetate (I) with $KHCO_3$ in methanol yielded a monoacetate after crystallization from ether: mp 89–90 °C; ^{1}H NMR δ 3.43 (dd, J = 5, 10 Hz, 1 H) and 2.0 (s, 3 H). The rest of the spectrum was similar to the diacetate with peaks at δ 4.7 and 2.1 absent.

Acknowledgments. This work was supported in part by Contract NO 1-CM-3-3750 from the Division of Cancer Treatment, National Cancer Institute, National Institutes of Health, the Elsa U. Pardee Foundation, Midland, Michigan, Grant CA10944 from the National Cancer Institute, and the University of Arizona Computer Center.

Registry No.—1, 64784-78-7; 1 monoacetate, 64784-79-8.

Supplementary Material Available: Tables of atomic coordinates of hydrogen atoms, temperature factors, bond distances, bond angles, and torsion angles, and packing diagram (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Identification was confirmed by Dr. Robert E. Perdue, Medicinal Plant Resources Laboratory, Agricultural Research Center, Beltsville, Md. A reference specimen was deposited in that herbarium. The plant was collected in Kenya, in June 1973.
(2) K. Morikawa and Y. Hirose, *Tetrahedron Lett.*, 1799 (1969).
(3) Carbon and hydrogen analysis were performed by Chemalytics, Inc., Tempe, Arizona. ^{1}H NMR and mass spectra were determined using a Varian T-60 spectrometer and Hewlett-Packard Model 5930 spectrometer, respectively. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.
(4) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(5) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).
(6) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr., Sect. B*, **17**, 1040 (1964).

Synthesis and Chemistry of Ethyl 2-Diethylphosphonoacrylate

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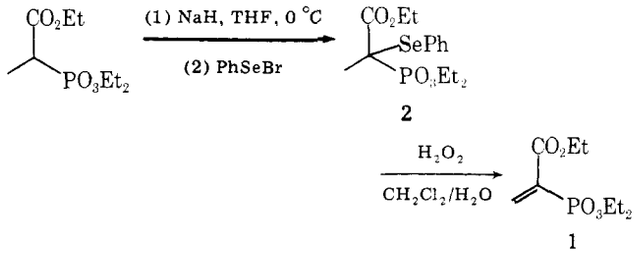
Received August 16, 1977

In recent years, vinyl phosphonium salts have found wide applicability in organic synthesis.[1] To date, numerous examples have been provided which demonstrate the utility of these reagents in the synthesis of acyclic,[1a] carbocyclic,[1b,f] and heterocyclic molecules[1c-e] containing carbon–carbon double bonds.

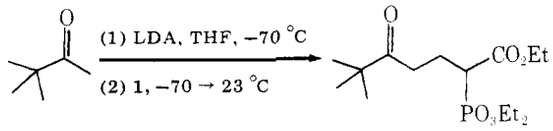
In contrast to the field of vinyl phosphonium salt chemistry, little attention has been given to the study of the synthesis and chemistry of vinyl phosphonates. Although reports of the synthesis of a few vinyl phosphonates have appeared in the literature,[2] the synthetic utility of these reagents has not been explored. Herein we describe a new synthesis of ethyl 2-diethylphosphonoacrylate (1)[2b] and reactions of this compound with a variety of anionic nucleophiles to produce stabilized phosphonate anions capable of undergoing subsequent reaction with aldehydes and ketones to produce unsaturated esters.

We chose to explore the possibility of using a selenoxide elimination as the method for generating the base-sensitive



unsaturation in **1**, due to the mildness of the reaction conditions necessary to achieve this transformation.[3] In fact, reaction of ethyl 2-diethylphosphonopropionate with sodium hydride followed by treatment with phenylselenyl bromide affords the selenylated derivative **2**, which is used without purification in the subsequent oxidation and elimination to give vinyl phosphonate **1** in an overall yield of 82%.

When vinyl phosphonate **1** is added slowly to a solution of the lithium enolate of pinacolone generated at −70 °C with lithium diisopropylamide (LDA) followed by slow warming to room temperature, keto ester phosphonate **3** is obtained in



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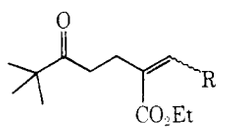
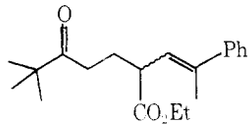
70% yield. If after warming to room temperature the intermediate phosphonate anion is allowed to react with an aldehyde or a ketone at reflux, unsaturated esters are isolated in good yield. Thus, reactions with benzaldehyde, propionaldehyde, 2-phenylpropionaldehyde, and cyclohexanone produce unsaturated esters **4, 5, 6** and **7** (~4:1 ratio), and **8** and **9** (~1:1 ratio) in 70, 78, 80, and 54% yields, respectively. We



4, R = Ph
5, R = CH_2CH_3
6, R = $CH(CH_3)Ph$



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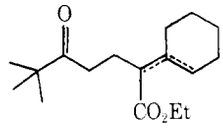

8, α,β isomer
9, β,γ isomer

were unable to obtain any appreciable yield of α,β-unsaturated ester in attempts to react the intermediate phosphonate anion with pivalaldehyde.

Similarly, reaction of the lithium enolates of 3-pentanone and *tert*-butyl acetate with vinyl phosphonate **1** followed by treatment of the resulting phosphonate anion with benzaldehyde at reflux furnishes α,β-unsaturated esters **10** and **11** in 74 and 69% yields, respectively. Treatment of the lithiated derivative of 1,3-dithiane[4] under analogous conditions affords α,β-unsaturated ester **12** in about 40% yield. All attempts to perform the analogous reaction using a 2-substituted 1,3-dithiane (i.e., 2-ethyl-1,3-dithiane) were uniformly unsuccessful.

Unsaturated esters **4, 5, 6, 7, 10, 11,** and **12** were isolated as a mixture of stereoisomers. The approximate ratios of these isomers were determined by integration of the appropriate vinyl proton resonances and (where necessary) by a comparison of the intensities of the characteristic resonances corre-

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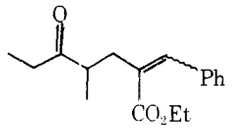
Table I. Stereochemical Results of the Reaction of Anions of Various Compounds with Vinyl Phosphonate 1 and Subsequent Reaction of Resultant Phosphonate Anions with Carbonyl Compounds

Carbanion precursor	Registry no.	Aldehyde or ketone	Registry no.	Products	Registry no.	Ratio	^{1}H-NMR chemical shift of vinyl resonances, δ values (multiplicity)
t-BuCOMe	75-97-8	PhCHO	100-52-7	(*E*)-**4**	64739-78-2	2	7.61 (s)
				(*Z*)-**4**	64739-79-3	1	7.20 (s)
t-BuCOMe		CH_3CH_2CHO	123-38-6	(*E*)-**5**	64739-86-2	1	6.68 (t)
				(*Z*)-**5**	64754-30-9	1	5.92 (t)
				(*E*)-**6**	64739-87-3	1	6.85 (d)
t-BuCOMe		$CH_3CH(Ph)CHO$	93-53-8	(*Z*)-**6**	64739-88-4	7	5.98 (d)
				(*E*)-**7**	64739-89-5	1	7.2–7.0 (unresolved)
				(*Z*)-**7**	64739-90-8	1	7.2–7.0 (unresolved)
Et_2CO	96-22-0	PhCHO		(*E*)-**10**	64739-91-9	1	7.75 (s)
				(*Z*)-**10**	64739-92-0	2	7.25 (s)
$MeCO_2$-*t*-Bu	540-88-5	PhCHO		(*E*)-**11**	64754-31-0	1	7.67 (s)
				(*Z*)-**11**	64739-93-1	1	7.22 (s)
$C_4H_8S_2$	505-23-7	PhCHO		(*E*)-**12**	64739-94-2	1	7.73 (s)
				(*Z*)-**12**	64739-95-3	3	7.23 (s)

sponding to the absorption due to the methylene group of the ethyl ester functionality in the ^{1}H-NMR spectrum (i.e., in the case of compounds **6** and **7**; see Table I). It can be expected that the chemical shift of the vinyl resonance in the (*E*)-unsaturated ester will occur at lower field than that observed for the corresponding (*Z*) isomer.[5] Typically, the difference in



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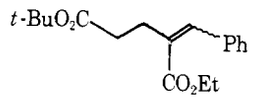

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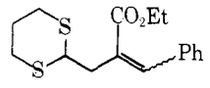

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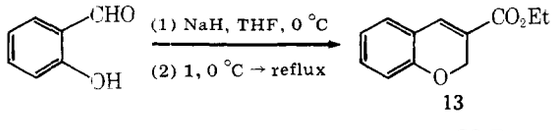
chemical shift is observed to be on the order of 0.4–0.8 ppm. The presence of the β,γ isomer (**9**) is indicated by the presence of a vinyl proton resonance and two resonances corresponding to the ethyl group of the ester functionality in the ^{1}H-NMR spectrum. None of these examples displayed a high degree of stereoselectivity in the olefin-forming reaction. From an examination of the data presented in Table I, no general conclusion can be drawn regarding the origin of the stereochemical outcome of these Wadsworth–Emmons reactions.

In order to make a comparison of the synthetic utility of vinyl phosphonate **1** as compared to that of vinyl phosphonium salts, compound **1** was used in two annelation reactions to form heterocyclic compounds. When the sodium salt of salicylaldehyde is allowed to react with **1** at 0 °C followed by reaction at reflux in THF, the 2*H*-1-benzopyran **13** is isolated in 78% yield. However, we were totally unsuccessful in our attempts to extend this reaction to a similar system by employing the sodium salt of 2′-hydroxyacetophenone. Under analogous conditions, the dihydrofuran **14** is obtained in 39% yield from 2-hydroxycyclohexanone.



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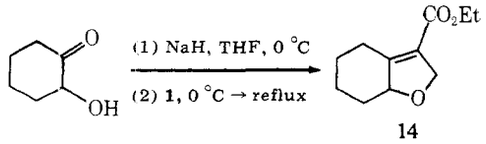

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We have demonstrated that various carbanionic nucleophiles are capable of undergoing Michael addition to vinyl phosphonate **1**, and the intermediate stabilized phosphonate anions react with a number of carbonyl compounds to form unsaturated esters in moderate to good yields. Unfortunately, the stereoselectivity in the reaction to form olefins is disappointingly low. In some systems where the β,γ-unsaturated ester is comparable in thermodynamic stability to the α,β isomer, some isomerization to the former is observed. Finally, vinyl phosphonate **1** has been shown to be of synthetic use for the production of some heterocyclic α,β-unsaturated esters.

Experimental Section

All boiling points are uncorrected. IR spectra were determined with a Perkin-Elmer Model 137 or Model 735 infrared recording spectrophotometer. ^{1}H-NMR spectra were determined at 60 MHz with a Varian Model T-60 NMR spectrometer. The chemical shift values are expressed in δ values (ppm) relative to tetramethylsilane as an internal standard. Significant ^{1}H-NMR data are tabulated in parentheses in the order (number of protons, multiplicity, proton assignments). Mass spectra were obtained with Varian MS-12, Varian M-66, and Consolidated 21-110B mass spectrometers. Mass spectra are given as *m/e* with relative intensities in parentheses. Gas–liquid partition chromatograph (GLC) analyses were performed on a Varian Aerograph 90-P instrument. Elemental analyses were performed by the Microanalytical Laboratory, operated by the College of Chemistry, University of California, Berkeley, Calif.

All reactions involving strong bases or organometallic reagents were performed under a nitrogen atmosphere. Ethereal solvents were dried by distillation from $LiAlH_4$ or sodium/benzophenone just prior to use. Diisopropylamine was dried by distillation from CaH_2 prior to use. Commercial solutions of *n*-butyllithium in hexane (Alfa Inorganics, Inc. or Foote Mineral Co.) were standardized by procedures of Watson and Eastham or Kofron and Baclawski.[6] All aldehydes and ketones used as starting materials were purified by distillation prior to use. 1,3-Dithiane was purified by sublimation.

Ethyl 2-Diethylphosphonoacrylate (1). To a suspension of 7.20 g (0.150 mol) of a 50% oil dispersion of NaH, washed free of oil with dry pentane, in 300 mL of dry THF at 0 °C is added dropwise 23.8 g (0.100 mol) of ethyl 2-diethylphosphonopropionate in 20 mL of dry THF. After the addition, the reaction mixture is stirred at 0 °C for 1.5 h. To the reaction mixture is added a solution of phenylselenyl bromide generated from 18.8 g (60 mmol) of diphenyldiselenide and 9.60 g (60 mmol) of bromine in 50 mL of dry THF. The reaction mixture is stirred for 1 min and poured into a mixture of 250 mL of saturated aqueous $NaHCO_3$, 500 mL of 50% ether/pentane, and ice. The aqueous phase is extracted with 500 mL of 50% ether/pentane, and the combined organic phases are washed with saturated aqueous NaCl solution and dried over Na_2SO_4. Evaporation yields 40.1 g of red-orange liquid which has spectral properties consistent with ethyl 2-diethylphosphono-2-phenylselenylpropionate (**2**): IR (thin film) 1730 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.8–7.0 (5 H, unresolved multiplets, aryl H's), 4.5–3.8 (6 H, unresolved multiplets, CH_2), 1.7–1.0 (12 H, unresolved multiplets, CH_3).

To a solution of 40.1 g of crude **2** in 300 mL of methylene chloride at 0 °C is added 28.3 g (0.25 mol) of 30% H_2O_2 in 25 mL of water over a 15-min period. The reaction mixture is stirred at 0 °C for 1 h, warmed to room temperature and stirred for an additional 2.5 h, then poured into a mixture of 250 mL of CH_2Cl_2 and 100 mL of 10% aqueous Na_2CO_3 solution. The aqueous layer is extracted with 250 mL of CH_2Cl_2, and the combined organic layers are washed with saturated aqueous NaCl solution and dried over Na_2SO_4. Evaporation and distillation in vacuo through a 15-cm Vigreaux column afford 19.6 g (82%) of **1** as a slightly yellow liquid, bp 88–90 °C (0.3 Torr): IR (thin film) 1720 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.03 (1 H, d of d, J = 2 and 25 Hz, vinyl H trans to phosphonate), 6.50 (1 H, d of d, J = 2 and 4 Hz, vinyl H cis to phosphonate), 4.5–3.8 (6 H, unresolved multiplets, CH_2), 1.45 (9 H, t, CH_3); mass spectrum 236 (1.7, M^+), 191 (48), 164 (31), 163 (66), 162 (55), 135 (100). Anal. Calcd for $C_9H_{17}O_5P$: C, 45.77; H, 7.25; P, 13.11. Found: C, 45.68; H, 7.14; P, 13.11.

6-Diethylphosphono-2,2-dimethyl-6-ethoxycarbonyl-3-hexanone (3). To a solution of 304 mg (3.00 mmol) of diisopropylamine in 4 mL of dry THF at 0 °C is added dropwise 1.34 mL (3.00 mmol) of 2.24 M n-BuLi in hexane. After 10 min the solution is cooled to −70 °C, and 300 mg (3.00 mmol) of pinacolone is added dropwise over a 3-min period. After 30 min, 709 mg (3.00 mmol) of **1** is added dropwise over a 20-min period by means of a syringe pump. The solution is stirred at −70 °C for 30 min and then warmed to room temperature. A 3-mL sample of saturated aqueous NH_4Cl is added, and the reaction mixture is diluted with water and extracted three times with ether. The combined ether extracts are dried over Na_2SO_4 and evaporated to afford 0.906 g of reddish liquid. Kugelrohr distillation in vacuo gives 704 mg (70%) of **3** as a clear liquid (oven temperature, 105–111 °C (0.3 Torr)): IR (thin film) 1730, 1705 cm^{-1}; ^{1}H-NMR (CCl_4) δ 4.12 (4 H, m, $POCH_2$), 3.98 (2 H, q, $COOCH_2$), 2.85 (1 H, d of t, J = 7 and 22 Hz, CH), 2.57 (2 H, t, aliphatic CH_2), 2.3–1.7 (2 H, unresolved multiplet, aliphatic CH_2), 1.32 (6 H, t, $POCH_2CH_3$), 1.25 (3 H, t, $COOCH_2CH_3$), 1.12 (9 H, s, Me_3C); HRMS 336.1746 (1.2, M^+ calcd for $C_{15}H_{29}O_6P$: 336.1708), 279 (100), 224 (18), 205 (17), 57 (35). Anal. Calcd for $C_{15}H_{29}O_6P$: C, 53.56; H, 8.69. Found: C, 53.56; H, 8.66.

6,6-Dimethyl-2-ethoxycarbonyl-1-phenyl-1-hepten-5-one (4). Reaction of the stabilized phosphonate anion derived from **3** generated as described above with 318 mg (3.00 mmol) of benzaldehyde at reflux for 30 min, quenching by addition of 3 mL of saturated aqueous NH_4Cl, dilution with water, extraction with ether, drying the ether extracts over Na_2SO_4, evaporation and Kugelrohr distillation in vacuo afford 604 mg (70%) of a 2:1 mixture of (*E*)-**4**/(*Z*)-**4** as a nearly colorless liquid (oven temperature, 85–90 °C (1 Torr)): IR (thin film) 1700, 1640 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.61 (0.67 H, s, vinyl H of (*E*) isomer), 7.35 (5 H, s, aryl H's), 7.20 (0.33 H, s, vinyl H of (*Z*) isomer), 4.23 (2 H, q, $COOCH_2$), 2.70 (4 H, broad, aliphatic CH_2), 1.33 (3 H, t, $COOCH_2CH_3$), 1.15 (9 H, s, Me_3C); HRMS 288.1742 (43, M^+ calcd for $C_{18}H_{24}O_3$: 288.1730), 231 (25), 186 (73), 185 (38), 129 (59), 115 (73), 57 (100). Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.64 H, 8.10.

2,2-Dimethyl-6-ethoxycarbonyl-6-nonen-3-one (5). Reaction of the stabilized phosphonate anion derived from **3**, generated as described above, with 174 mg (3.00 mmol) of propionaldehyde at reflux for 1.25 h, work-up, and Kugelrohr distillation afford 561 mg (78%) of a 1:1 mixture of (*E*)-**5**/(*Z*)-**5** as a clear liquid (oven temperature, 85–90 °C (0.5 Torr)): IR (thin film) 1710 cm^{-1}; ^{1}H-NMR (CCl_4) δ 6.68 (0.5 H, t, vinyl H of (*E*) isomer), 5.92 (0.5 H, t, vinyl H of (*Z*) isomer), 4.18 and 4.15 (2 H, q, $COOCH_2$), 3.7–2.0 (6 H, unresolved multiplets, aliphatic CH_2), 1.28 (3 H, t, $COOCH_2CH_3$), 1.17 (3 H, t, aliphatic CH_3), 1.12 (9 H, s, Me_3C); HRMS 240.1730 (5.2, M^+ calcd for $C_{14}H_{24}O_3$: 240.1725), 183 (65), 155 (47), 81 (46), 57 (100). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.59; H, 10.06.

2,2-Dimethyl-6-ethoxycarbonyl-8-phenyl-6-nonen-3-one (6). Reaction of the phosphonate anion derived from **3**, generated as described above, with 402 mg (3.00 mmol) of 2-phenylpropionaldehyde at reflux for 3.5 h, work-up, and Kugelrohr distillation in vacuo afford 765 mg (80%) of a 7:1:1:1 mixture of (*Z*)-**6**/(*E*)-**6**/(*Z*)-**7**/(*E*)-**7** as a pale yellow liquid (oven temperature, 120–125 °C (0.4 Torr)): IR (thin film) 1710 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.18 (5 H, s, aryl H's), 7.2–7.0 (0.2 H, unresolved multiplets, vinyl H of (*Z*)-**7** and (*E*)-**7**), 6.85 (0.1 H, d, vinyl H of (*E*)-**6**), 5.98 (0.7 H, d, vinyl H of (*E*)-**6**), 5.98 (0.7 H, d, vinyl H of (*Z*)-**6**), 4.53, 4.21, and 4.10 (0.6 H, q, $COOCH_2$ of (*E*)-**6**, (*E*)-**7**, and (*Z*)-**7**), 4.16 (1.4 H, q, $COOCH_2$ of (*Z*)-**6**), 2.53 (5 H, unresolved multiplets, aliphatic CH_2 and benzylic H), 1.6–1.0 (6 H, unresolved multiplets, $COOCH_2CH_3$ and benzylic CH_3), 1.05 (9 H, s, Me_3C); HRMS 316.2016 (4.2, M^+ calcd for $C_{20}H_{28}O_3$: 316.2044), 270 (62), 171 (100), 159 (43), 143 (72), 129 (41), 105.0695 (46), 105.0341 (57), 77 (46), 57 (91). Anal. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.42; H, 8.76.

6-Cyclohexylidene-2,2-dimethyl-6-ethoxycarbonyl-3-hexanone (8). Reaction of the phosphonate anion derived from **3**, generated as described above, with 294 mg (3.00 mmol) of cyclohexanone at reflux for 25 h, work-up, and Kugelrohr distillation in vacuo afford 451 mg (54%) of a 1:1 mixture of **8** and its β,γ-unsaturated isomer (**9**) as a pale yellow liquid (oven temperature, 95–100 °C (0.4 Torr)): IR (thin film) 1710 cm^{-1}; ^{1}H-NMR (CCl_4) δ 5.55 (0.5 H, multiplet, vinyl H of **9**), 4.13 and 4.04 (2 H, q, $COOCH_2$), 2.9–1.0 (13.5 H, unresolved multiplets, aliphatic and cyclohexyl CH_2's), 1.30 and 1.27 (3 H, t, $COOCH_2CH_3$), 1.12 (9 H, s, Me_3C); HRMS 280.2002 (4.2, M^+ calcd for $C_{17}H_{28}O_3$: 280.2038), 168 (81), 153 (41), 57 (100). Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.07. Found: C, 72.50; H, 9.79.

6-Ethoxycarbonyl-4-methyl-7-phenyl-6-hepten-3-one (10). A THF solution of the enolate derived from 258 mg (3.00 mmol) of 3-pentanone by reaction with 3.00 mmol of LDA at −78 °C is treated with 3.00 mmol of compound **1** (as described above) to generate the phosphonate anion. Reaction with 318 mg (3.00 mmol) of benzaldehyde at reflux for 45 min, work-up, and Kugelrohr distillation in vacuo afforded 612 mg (74%) of a 2:1 mixture of (*Z*)-**10**/(*E*)-**10** as a slightly yellow liquid (oven temperature, 105–110 °C (0.3 Torr)): IR (thin film) 1710 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.75 (0.33 H, s, vinyl H of (*E*) isomer), 7.40 (5 H, s, aryl H's), 7.25 (0.67 H, s, vinyl H of (*Z*) isomer), 4.25 (1.34 H, q, $COOCH_2$ of (*Z*) isomer), 4.08 (0.66 H, q, $COOCH_2$ of (*E*) isomer), 3.1–2.0 (3 H, unresolved multiplets, aliphatic CH and CH_2), 2.33 (2 H, q, aliphatic CH_2), 1.35 (3 H, t, $COOCH_2CH_3$), 0.98 (3 H, t, aliphatic CH_3); HRMS 274.1535 (38, M^+ calcd for $C_{17}H_{22}O_3$: 274.1569), 229 (44), 172 (41), 117 (48), 115 (66), 57 (100). Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.04; H, 8.10.

***tert*-Butyl 4-Ethoxycarbonyl-5-phenyl-4-pentenoate (11).** A THF solution of the enolate derived from reaction of 348 mg (3.00 mmol) of *tert*-butyl acetate by reaction with 3.00 mmol of LDA at −78 °C is treated with 3.00 mmol of compound **1** (as described above) to generate the phosphonate anion. Reaction with 318 mg (3.00 mmol) of benzaldehyde at reflux for 45 min, work-up, and Kugelrohr distillation in vacuo gives 629 mg (69%) of a 1:1 mixture of (*E*)-**11**/(*Z*)-**11** as a nearly colorless liquid (oven temperature, 105–110 °C (0.5 Torr)): IR (thin film) 1725, 1710 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.67 (0.5 H, s, vinyl H of (*Z*) isomer), 4.25 (2 H, broad q, $COOCH_2$), 3.0–1.9 (4 H, unresolved multiplets, aliphatic CH_2), 1.43 (9 H, s, Me_3C), 1.30 (3 H, t, $COOCH_2CH_3$); HRMS 248.1044 (53, M^+ calcd for $C_{18}H_{24}O_4$–C_4H_8: 248.1051), 202 (43), 174 (54), 129 (85), 115 (50), 57 (100). Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 70.61; H, 7.89.

2-(2-Ethoxycarbonyl-3-phenyl-2-propenyl)-1,3-dithiane (12). To a solution of 361 mg (3.00 mmol) of 1,3-dithiane in 6 mL of dry THF at −40 °C is added dropwise 1.40 mL (3.15 mmol) of 2.24 M n-BuLi in hexane. The solution is stirred for 1.5 h at −40 to −20 °C and cooled to −70 °C, and 709 mg (3.00 mmol) of compound **1** is added dropwise over a 20-min period by means of a syringe pump. The solution is warmed to room temperature, and 318 mg (3.00 mmol) of benzaldehyde is added. The reaction solution is then refluxed for 45 min, cooled to room temperature, and quenched by addition of 3 mL of saturated aqueous NH_4Cl. The resulting mixture is diluted with water and extracted three times with ether. The combined ether extracts are dried over Na_2SO_4 and evaporated. The residue is Kugelrohr distilled in vacuo to afford 645 mg of viscous yellow liquid (oven temperature, 103–108 °C (10^{-3} Torr)), which by NMR was 2:1 mixture of **12** and an unknown compound (~40% yield of **12**). An analytically pure sample of a 3:1 mixture of (*Z*)-**12**/(*E*)-**12** was obtained by preparative GLC (8% SE-30, 5 ft × 0.25 in. 255 °C, retention time 3.2 min): IR (thin film) 1695, 1620 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.73 (0.25 H, s, vinyl H of (*E*)-**12**), 7.40 (5 H, s, aryl H's), 7.23 (0.75 H, s, vinyl H of (*Z*)-**12**), 4.5–3.9 (3 H, unresolved multiplets, $COOCH_2$ and SCHS), 3.1–2.5 (6 H, unresolved multiplets, SCH_2 and allylic CH_2), 2.2–1.6 (2 H, unresolved multiplets, CH_2), 1.37 (2.25 H, t, $COOCH_2CH_3$ of (*Z*)-**12**), 1.03 (0.75 H, t, $COOCH_2CH_3$ of (*E*)-**12**); mass spectrum 308 (2.4, M^+), 119 (100), 94 (15), 71 (16), 57 (27), 55 (20). Anal. Calcd for $C_{16}H_{20}O_2S_2$: C, 62.30; H, 6.54. Found: C, 62.34; H, 6.54.

3-Ethoxycarbonyl-2*H*-1-benzopyran (13). To a suspension of 172 mg (3.60 mmol) of a 50% oil dispersion of NaH, washed free of oil with dry pentane, in 10 mL of dry THF at 0 °C is added 366 mg (3.00 mmol) of salicylaldehyde dropwise over a 3-min period. After 2 h, 709 mg (3.00 mmol) of compound **1** is added dropwise over a 5-min period and the reaction mixture is warmed to room temperature and stirred for 2 h. The reaction mixture is then heated at 60–70 °C for 1.5 h, cooled to room temperature, diluted with water, and extracted three times with ether. The combined ether extracts are dried over Na_2SO_4 and evaporated to yield a green liquid. Kugelrohr distillation in vacuo gives 470 mg (78%) of **13** as a clear liquid (oven temperature, 108–114 °C (2 Torr)): IR (thin film) 1710 cm^{-1}; ^{1}H-NMR (CCl_4) δ 7.4–6.6 (5

H, unresolved multiplets, aryl H's and vinyl H), 4.91 (2 H, d, J = 2 Hz, CH_2O), 4.20-(2 H, q, $COOCH_2$), 1.30 (3 H, t, $COOCH_2CH_3$); HRMS 204.0771 (34, M^+ calcd for $C_{12}H_{12}O_3$: 204.0788), 175 (100), 131 (89), 77 (28). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.26; H, 5.94.

9-Ethoxycarbonyl-7-oxabicyclo[4.3.0]-1(9)-nonene (14). To a suspension of 144 mg (3.00 mmol) of a 50% oil dispersion of NaH, washed free of oil with dry pentane, in 5 mL of dry THF at 0 °C is added 432 mg (3.78 mmol) of freshly distilled 2-hydroxycyclohexanone dropwise over a 3-min period. After 1 h, 709 mg (3.00 mmol) of compound 1 is added dropwise over a 20-min period by means of a syringe pump. The reaction solution is refluxed for 24 NH_4Cl, diluted with water, and extracted and dried over Na_2SO_4, evaporated, and chromatographed on silica gel, eluting with ethyl acetate/hexane (2:6, v/v), to afford 230 mg (39%) of **14** (R_f 0.40 eluting with 40% EtOAc/hexane) as a clear liquid: IR (thin film) 1710 cm^{-1}; ^{1}H-NMR (CCl_4) δ 4.63 (2 H, broad, CH_2O), 4.13 (2 H, q, $COOCH_2$), 3.7–3.3 (1 H, unresolved multiplet, CHO), 2.4–1.0 (8 H, unresolved multiplets, cyclohexyl H's), 1.28 (3 H, t, $COOCH_2CH_3$); HRMS 196.1057 (35, M^+ calcd for $C_{11}H_{16}O_3$: 196.1099), 194 (41), 151 (53), 150 (71), 123 (100), 122 (41). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 66.83; H, 8.17.

Acknowledgments. Support for this research was provided by funds from the National Science Foundation (Grant No. GP-31321X) and the National Institutes of Health (Grant No. CA-12617). We thank Professor Martin Semmelhack for informing us of his similar research with compound 1 prior to publication [see accompanying note].

Registry No.—**1**, 20345-61-3; **2**, 64739-80-6; **3**, 64739-81-7; **8**, 64739-82-8; **9**, 64739-83-9; **13**, 57543-58-5; **14**, 64739-84-0; ethyl 2-diethylphosphonopropeionate, 3699-66-9; phenylselenyl bromide, 34837-55-3; cyclohexanone, 108-94-1; salicylaldehyde, 90-02-8; 2-hydroxycyclohexanone, 533-60-8; i, 64739-85-1.

References and Notes

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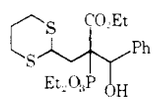
(7) The unknown compound was not distinguishable by TLC from **12** and was not detectable by GLC. From the fact that the ^{1}H-NMR spectrum of the product after Kugelrohr distillation contained an additional aromatic singlet and absorptions characteristic of the methylene protons of a diethylphosphonate functional group, and that the IR spectrum showed a weak OH stretching absorption, the unknown compound was postulated to have structure i.



i

Preparation of 2-(Alkylthiomethyl)acrylates

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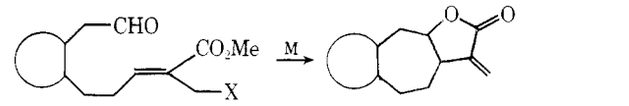
Received August 23, 1977

The synthesis of trisubstituted alkenes has been an active area of study in recent years; many general strategies are now available.[1] We are pursuing a plan for synthesis of the sesquiterpene α-methylene-γ-lactones which utilizes intramolecular Reformatsky-type reaction[2] and necessitates the preparation of the 2-substituted acrylate unit as in **1**. Previously developed stereospecific methods were applied to simple systems related to **1** with some success but required



1, X = Br, OH, SR + MeO—M—X

M = metal

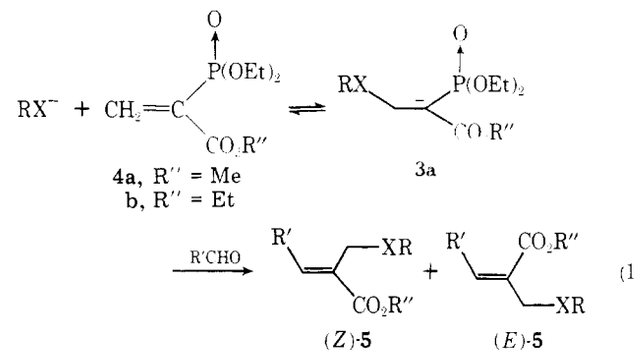
several steps, some involving vigorous reaction conditions.[2] Here we report a method for preparation of the desired acrylate unit under mild conditions and with high efficiency. The method is based on Wittig reagents of the sort represented by **2** and **3**. A general technique for preparation of phosphorus reagents such as **2b** is due to Corey[3] and to Schlosser,[4] but we have failed in our attempts to apply that method in preparation of **2a** (X = OH) or **3a** (X = OH). Apparently, reaction of

2a, R = CO_2Me; X = OH
b, R = alkyl; X = OH

3a, R = CO_2Me; X = OH
b, R = alkyl; X = OH

2a or **3a** with an aldehyde is slower than elimination of Ph_3PO (from **2a**) and $HOP(O)(OMe)_2$ (from **3a**). With other heteroatom units X in **2a** and **3a** (e.g., X = acetate), elimination of X^- is invariably too rapid.

Nevertheless, we expected that the elimination of X^- could be reversible, still providing useful concentrations of **2a** and **3a**. After a series of unsuccessful experiments with oxygen anions (in eq 1), the thiolate anion (X = S) was found to lead



4a, R'' = Me
b, R'' = Et

3a

(Z)-5 (E)-5 (1)

to the desired conversion. The requisite methyl 2-(diethylphosphono)acrylate **4** was prepared according to the procedure of Pudovik,[5] which is presented in detail in the Experimental Section. The yield of **4** was only moderate, but the procedure is direct, and the reagent can be prepared on large scale, distilled, and stored for later use. Then addition of **4** to a suspension of sodium hydride and the thiol in tetrahydrofuran, followed by an aldehyde (stirring for 2.0 h at 25 °C), affords the 2-(alkylthiomethyl)acrylate (**5**) in high yield.

Table I displays the results of experiments designed to test the effects of solvent polarity, cation type, and structure of the organic unit in the thiolate anion on the efficiency and the stereochemical outcome of the reaction. In this case n-heptanal, phosphonoacrylate **4b**, and a thiolate anion were allowed to react under a variety of conditions. The yield of combined E and Z isomers was high in every case.[6]

The data in Table I demonstrate that the ratio of isomers depends upon counterion, solvent, and the nature of the thiolate anion, although no useful correlation is evident. The

