$Pd(PPh_3)_4$ (84 mg, 0.073 mmol) in THF (1.5 mL) and heating for 50 min in a 45 °C oil bath. The reaction was quenched by the addition of brine. The aqueous phase was repeatedly extracted with ether, and the combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material (96 mg) was chromatographed over SiO_2 (14 g) with hexane–ethyl acetate (2:1) to provide a 4:1 ratio of adduct **4g** and its trans-1,4 isomer (40 mg, 44% yield). Although the dark yellow oil is unstable, it tolerates bulb-to-bulb distillation temperatures of 40–58 °C at 0.10 mmHg: R_f 0.31 (2:1 hexane–ethyl acetate); $[\alpha]^{26}_D$ +146.4° (*c* 1.725, $CHCl_3$); ^1H NMR δ 1.66 (dt, J = 14.6 and 3.9 Hz, 1 H, β-CH_2), 1.70 (overlapping br s, 1 H, O*H*), 2.72 (overlapping dt, J = 14.6 and 7.3 Hz, 1 H, α-CH_2), 4.22 (m, 1 H, C*H*N_3), 4.74 (m, 1 H, C*H*OH), 5.92 and 6.09 (2 m, 2 × 1 H, C*H*=C*H*); ^{13}C NMR δ 40.0, 64.6, 75.0, 132.1, 138.0; IR (neat) 3327 (OH), 2947, 2108 (N_3) cm^{-1}.

(+)-(1*S*,4*R*)-4-Phthalimido-2-cyclopenten-1-ol (4h) was prepared from the commercially available potassium phthalimide salt. The crude product was chromatographed over SiO_2 with methylene chloride–methanol–ammonium hydroxide (82:15:3) to provide a colorless solid in 74% yield. Recrystallization from ether afforded crystals of uniform melting point: mp 69–71 °C; R_f 0.47 (1:1 hexane–ethyl acetate); $[\alpha]^{26}_D$ +276° (*c* 1.03, $CHCl_3$); ^1H NMR δ 1.97 (br d, J = 15.4 Hz, 1 H, β-CH_2), 2.82 (ddd, J = 15.4, 9.6 and 7.8 Hz, 1 H, α-CH_2), 4.07 (br s, 1 H, O*H*), 4.74 (m, 1 H, C*H*OH), 5.23 (m, J = 9.6 and 2.2 Hz, 1 H, C*H*-N), 5.72 (dd, J = 5.5 and 2.5 Hz, 1 H, C=C*H*), 6.22 (m, J = 5.5, 1 H, C=C*H*), 7.65–7.90 (m, 4 H, Ar); ^{13}C NMR δ 38.2, 53.0, 75.8, 123.3, 130.1, 131.8, 134.2, 138.4, 168.4; IR (KBr) 3398 (OH), 1697 (C=O), 1380, 720 cm^{-1}. Anal. Calcd for $C_{13}H_{11}O_3N$: C, 68.12; H, 4.84; N, 6.11. Found: C, 67.81; H, 4.81; N, 6.31.

(+)-(1*S*,4*S*)-Methyl (4-Hydroxy-2-cyclopenten-1-yl)acetate (7). To an ice-cold suspension of anhydrous Na_2HPO_4 (42 mg) and adduct **4c** (421 mg, 1.42 mmol) in dry MeOH (8.0 mL) was added approximately 0.5% Na(Hg) previously prepared by mixing mercury (10 g) with sodium (50 mg, 2.17 mmol). The stirred reaction mixture was held at 0 °C until TLC analysis (R_f 0.22; 1:1 hexane–ethyl acetate) indicated the starting material was consumed (1.5 h). The methanolic solution was transferred to a separatory funnel, diluted with ether, and washed with water. The aqueous phase was sequentially extracted with ether until no product remained (TLC) in the water layer. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was chromatographed over SiO_2 (50 g, 1.5:1 hexane–ethyl acetate). Evaporation of solvent under vacuum provided 150 mg (67% yield) of oil. Subsequent bulb-to-bulb distillation between 80 and 100 °C at 0.15 mmHg afforded 128 mg of colorless material for analysis: R_f 0.40 (1:1 hexane–ethyl acetate); $[\alpha]^{22}_D$ +15.3° (*c* 2.29, $CHCl_3$); ^1H NMR δ 1.36 (dt, J = 13.9 and 7.8 Hz, 1 H, β-CH_2), 2.49 (m, J = 6.4 Hz, 2 H, CHC*H*$_2$CO$_2$), 2.53 (overlapping m, J = 13.9 and 4.8 Hz, 1 H, α-CH_2), 2.57 (overlapping br s, 1 H, O*H*), 2.95 (m, 1 H, C*H*CH$_2$CO$_2$), 3.65 (s, 3 H, CH_3), 4.78 (m, 1 H, C*H*OH), 5.79 (br s, 2 H, C*H*=C*H*); IR (neat) 3425 (OH), 2954, 1718 (C=O), 1439 cm^{-1}; MS *m/z* (relative intensity) 156 (M^+, 0.2), 138 (18), 96 (33), 83 (80), 79 (100); HRMS calcd for $C_8H_{12}O_3$ (M^+) 156.0786, found 156.0784.

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Note Added in Proof: A recent paper by Oppolzer et al. (*Tetrahedron Lett.* **1988**, *29*, 4705) reports a palladium-catalyzed substitution reaction on (1*R*,4*R*)-*trans*-1-acetoxy-4-chlorocyclopent-2-ene by the anion of a substituted malonate. Replacement of the allylic chloride proceeds with retention.

Registry No. **4a**, 120052-50-8; **4b**, 119971-14-1; **4c** (isomer 1), 119971-15-2; **4c** (isomer 2), 120052-52-0; **4d** (isomer 1), 119971-16-3; **4d** (isomer 2), 120052-53-1; **4e**, 120052-51-9; **4f**, 119971-17-4; (1*S*,4*R*)-**4g**, 120056-07-7; (1*S*,4*S*)-**4g**, 120056-08-8; **4h**, 119971-18-5; (+)-**5**, 60410-16-4; **7**, 120052-54-2; $CH_2(COCH_3)_2$, 123-54-6; $PhSO_2CH_2CO_2CH_3$, 34097-60-4; $CH_3COCH_2CO_2CH_3$, 105-45-3; PhOH, 108-95-2; PhSH, 108-98-5; PthK, 1074-82-4; sodium dimethyl malonate, 18424-76-5.

Low Temperature Nuclear Magnetic Resonance Study of the Acylation of a Stabilized Ylide: C- vs O-Acylation

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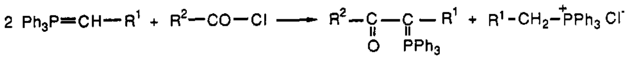
Acyl phosphoranes[1–4] and acyl phosphonium salts[4,5] produced from the reaction of an acid chloride with a phosphorus ylide continue to find use in organic synthesis. When ylides of the type **1** are used, a transylidation reaction occurs to produce the phosphonium salt **4** together with the synthetically useful acyl phosphorane **3**. Alternatively, the transylidation step can be suppressed by using low temperatures or by using substituted ylides, e.g., **5** and the thus-obtained phosphonium salts, e.g., **6a**, can be isolated.[4]

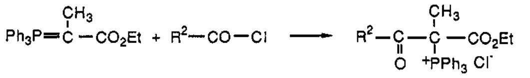


$$2\ Ph_3P{=}CH{-}R^1 + R^2{-}CO{-}Cl \longrightarrow R^2{-}\underset{O}{\underset{\|}{C}}{-}\underset{PPh_3}{\underset{\|}{C}}{-}R^1 + R^1{-}CH_2{-}\overset{+}{P}Ph_3\ Cl^-$$

1a, $R^1 = H$
1b, $R^1 = CH_3$
1c, $R^1 = Ph$
1d, $R^1 = CO_2Et$

2 **3** **4**

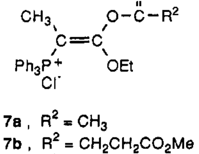
We now show by low-temperature NMR that the reaction of ylide **5** with an acid chloride, e.g., acetyl chloride, initially yields the unexpected and labile *O*-acyl phosphonium salt, e.g., **7a**, which readily rearranges to the corresponding *C*-acyl phosphonium salt, e.g., **6a**, on standing. Treatment of the latter phosphonium salt with either a second equivalent of ylide[4] or triethylamine[5] then yields the expected allene product.



$$Ph_3P{=}\overset{CH_3}{\overset{|}{C}}{-}CO_2Et + R^2{-}CO{-}Cl \longrightarrow R^2{-}\underset{O}{\underset{\|}{C}}{-}\overset{CH_3}{\overset{|}{\underset{^+PPh_3\ Cl^-}{\underset{|}{C}}}}{-}CO_2Et$$

5

6a, $R^2 = CH_3$
6b, $R^2 = CH_2CH_2CO_2Me$
6c, $R^2 = CH_2CH_2CO_2CH_2Ph$



7a, $R^2 = CH_3$
7b, $R^2 = CH_2CH_2CO_2Me$
7c, $R^2 = CH_2CH_2CO_2CH_2Ph$

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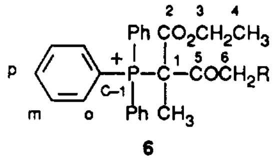
0022-3263/89/1954-2762$01.50/0

Table I. ^1H and Selected ^{13}C NMR Data for the *C*-Acyl and *O*-Acyl Phosphoranes



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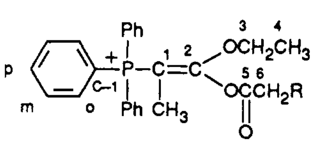

7

compound	carbon chemical shifts[a] C-1	o	m	p	1	1-CH_3	2	3	4	5	6
6a, R = H	117.7 (86.6)	134.6 (10.2)	130.4 (12.8)	135.3 (3.0)	66.3 (50.4)	21.6	166.5	64.8	13.3	201.3 (4.3)	28.7 (2.0)
6b, R = CH_2CO_2Me	116.5 (86.0)	132.9 (10.8)	129.3 (13.2)	134.3	64.8 (50.0)	20.5	164.7	63.8	12.1	201.2 (4.2)	34.2 (1.5)
6c, R = CH_2-CO_2CH_2Ph	117.7 (85.6)	134.0 (10.0)	130.3 (13.0)	135.3	66.1 (50.0)	21.6	165.9	64.9	13.2	202.1 (4.1)	35.2 (2.1)
7a, R = H	117.1 (91.7)	132.4 (10.0)	129.1 (12.8)	133.9	75.4 (93.5)	12.1 (7.5)	158.6 (12.0)	65.5	12.5	165.0	19.8
7b, R = CH_2CO_2Me	117.7 (91.6)	133.0 (10.4)	129.7 (12.8)	134.4 (2.9)	75.7 (93.4)	12.5 (7.3)	159.3 (12.1)	66.0	12.9	168.1	28.0

compound	proton chemical shifts[b] PPh_3	1-CH_3	3	4	6	7	9	Ph
6a, R = H	7.6–8.0	2.20 (d, 17.7)	4.15 (m)	1.10 (t, 7.1)	2.66			
6b, R = CH_2CO_2Me	7.6–8.0	2.20 (d, 18.0)	4.15 (m)	1.10 (t, 7.2)	3.25 (H_a, m) 3.47 (H_b, m)	2.66 (m)	3.64 (s)	
6c, R = $CH_2CO_2CH_2Ph$	7.6–8.0	2.11 (d, 16.2)	4.15 (m)	1.04 (t, 7.1)	3.22 (H_b, m) 3.40 (H_b, m)	2.72 (m)	5.06 (AB q, 12.6) 5.09	7.30
7a, R = H	7.40–8.00	1.65 (d, 14.5)	3.73 (q, 7.1)	0.53 (t, 7.1)	2.49 (s)			
7b, R = CH_2CO_2Me	7.40–7.90	1.67 (d, 14.7)	3.79 (q, 7.1)	0.54 (t, 7.1)	3.11 (m)	2.84 (m)	3.70 (s)	
7c, R = $CH_2CO_2CH_2Ph$	7.40–8.00	1.62 (d, 14.6)	3.75 (q, 7.1)	0.50 (t, 7.1)	3.12 (m)	2.88 (m)	5.13 (s)	7.30

[a] Chemical shifts in parts per million (^{13}C–^{31}P coupling constants in hertz). [b] Chemical shifts in parts per million (multiplicity, hertz).

Table II. ^{31}P Characterization[a]

compound	^{31}P NMR ($CDCl_2$): δ
6a	36.3
6b	36.0
7a	24.3
7b	24.3

[a] Chemical shifts relative to 85% H_3PO_4 standard.

Tables I and II list NMR data for the initially formed *O*-acyl phosphonium salts **7** and the ultimately formed *C*-acyl phosphonium salts **6**. The ^{13}C resonances were assigned on the basis of the chemical shifts and ^{13}C–^{31}P coupling constants of previously studied phenyl-substituted phosphorus compounds[6,7] and by using low temperature heteronuclear ^1H–^{13}C correlation spectroscopy.

The ^{13}C NMR spectral data for **6** and **7** are consistent with the assigned structures. Importantly, the aromatic C-1 resonance of both sets of compounds occurs in an upfield position characteristic of a phosphonium salt[6,7] and the expected ^{13}C–^{31}P coupling constants[6,7] are evident for the phenyl carbons. The ^{13}C NMR signal for carbon 1 in structures **7** is downfield relative to model compounds.[8]

Ylides of the type **5** have been shown to be equilibrium mixtures of cis and trans enolate forms which show separate ^1H and ^{13}C NMR signals.[6,9] Compound **7a** would appear to be a single isomer by ^1H NMR and ^{13}C NMR (−35 °C), and on the basis of the OCH_2CH_3 proton chemical shift,[9] the configuration of the *O*-acyl phosphoranes **7** is tentatively assigned as shown.

The broad band decoupled ^{31}P spectra for **6a**, **6b**, **7a**, and **7b** (Table II) gave the expected signals of tetravalent phosphorus in the range δ 20–40[10] (downfield relative to 85% H_3PO_4). No other intermediates were detected.

Reports of ylide alkylation,[11] triflations,[12] and acylations (aromatic acid chlorides only)[13] through oxygen have appeared, but the present study is unique in that the *O*-acyl species appear to be the precursors to the *C*-acyl compounds. Although presumably intramolecular, the exact mechanism for this conversion remains uncertain.

Experimental Section

Materials. Acetyl chloride and 3-carbomethoxypropionyl chloride were distilled prior to use, and 3-carbobenzoxypropionyl chloride was prepared from 3-carbobenzoxypropanoic acid[14] by using oxalyl chloride.[15] Ethyl 2-(triphenylphosphoranylidene)propionate (**5**) was recrystallized four times from ethyl acetate/petroleum ether.

NMR Spectroscopy. NMR spectra were recorded on a Varian XL300 spectrometer in dry $CDCl_3$. ^1H (300 MHz) and ^{13}C (75 MHz) spectra were routinely recorded at −10 °C and ^{31}P (122 MHz) spectra at +3 °C. For ^{31}P measurements, a 10-μs pulse, equivalent to a 45° flip angle, with broad-band decoupling was used. A $CDCl_3$ solution of ylide **5** (0.2 mM) in an NMR tube was cooled to 0 °C. One equivalent of the acid chloride was added, and the ^1H and ^{13}C NMR spectra were recorded at −10 °C. An external 85% H_3PO_4 standard was inserted, and the ^{31}P NMR spectra were recorded at 3 °C. The samples were warmed to room temperature, and the appearance of the *C*-acyl phosphonium salts **6** was monitored by ^1H, ^{31}P, and ^{13}C NMR spectroscopy.

Registry No. **5**, 5717-37-3; **6a**, 119946-77-9; **6b**, 119946-78-0; **6c**, 119946-79-1; **7a**, 119946-80-4; **7b**, 119946-81-5; **7c**, 119946-82-6; CH_3COCl, 75-36-5; $MeO_2CCH_2CH_2COCl$, 1490-25-1; $PhCH_2CO_2CH_2CH_2COCl$, 119946-83-7.

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