this property is the ability of the substituent to interact by resonance (overlap) and, in particular, by electron donation. The most reasonable acceptor of this electron back-donation would seem to be a $p\pi$–$d\pi$ bond as in resonance form **3**, but a number of other explanations are possible and these are being actively explored.

Experimental Section

Phospha-λ^5-azenes 1a–e were made by the Staudinger reaction using the appropriate azide and triphenylphosphine[13–15] and **1f** was made by the method of Horner.[15,16] The properties matched those reported. The NMR spectra were obtained on a Nicolet NT-200 wide bore spectrometer with a 4.7 T superconducting solenoid. ^{31}P spectra were taken at 80.99 MHz using an external 85% H_3PO_4 standard. The spectra were taken in $CDCl_3$ (12-mm tubes) at concentrations of 300 mg/3 mL, 200 mg/3 mL, 100 mg/3 mL, and 30 mg/3 mL and extrapolated to infinite dilution. Two level broad band proton decoupling was employed with a pulse angle of approximately 90° and a post acquisition delay of 1 s. Natural-abundance ^{15}N spectra were obtained at 20.28 MHz using gated broad band proton decoupling (decoupler on during acquisiton), a pulse angle of about 23°, and a post acquisition delay of 6 s. Samples were about 1.3–1.8 M in $CDCl_3$ and 20-mm tubes were employed. ^{15}N chemical shifts were measured using an external $K^{15}NO_3$ solution in H_2O which had been standardized against neat CH_3NO_2. The shifts relative to liquid NH_3 were calculated by using $\delta(NH_3) = \delta(CH_3NO_2) + 380.23$.[7]

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Registry No. **1a**, 14562-02-8; **1b**, 31641-65-3; **1c**, 2325-27-1; **1d**, 2327-67-5; **1e**, 14796-89-5; **1f**, 77116-68-8; **2a**, 100-01-6; **2b**, 106-47-8; **2c**, 62-53-3; **2d**, 106-49-0; **2e**, 104-94-9; **2f**, 99-98-9.

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Coupling Reactions of α-Halo Esters with Allyl- and Acetonyltin Reagents. An Improved Synthesis of α-Acetonyl-γ-butyrolactone

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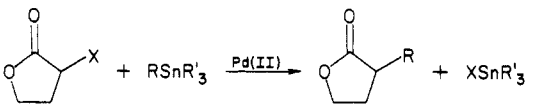
The palladium-catalyzed coupling reactions of organic electrophiles with organotin reagents provide a convenient, high yield pathway for carbon–carbon bond formation. The coupling reactions of acyl chlorides,[1] allyl chlorides and bromides,[2] and vinyl triflates[3] as the electrophilic partner take place with a wide variety of tin reagents under conditions that are mild enough that diverse functionality is acceptable in both coupling partners. Generally, in the reactions where an sp^3 carbon undergoes oxidative addition, β-hydrogens on an sp^3 carbon cannot be present in the electrophile but can be present in the organotin partner. This is because the product of oxidative addition with the electrophile is able to undergo β-hydride elimination.[4] Apparently the diorganopalladium(II) complex can have a β-hydrogen because the transmetalation step which follows oxidative addition of the electrophile to a palladium(0) complex is slow, while the 1,1-reductive elimination which follows the transmetalation is fast.[5] Surprisingly, however, α-bromo-γ-butyrolactone which possesses β-hydrogens was observed to cross-couple in good yield.

Coupling reactions of organotin reagents with α-halo esters have been reported using free radical conditions. However, high temperatures were required and only moderate yields were reported.[6] Milder reaction conditions and a greater variety of coupling partners might be expected when palladium catalysts are used, however. Consequently, it appeared to be worthwhile to attempt the coupling reaction of α-halo esters with various organotin reagents in the presence of a palladium catalyst.

The coupling reactions of α-bromo- and α-iodo-γ-butyrolactone with allyltin reagents and tributylacetonyltin were carried out under different conditions to give high yields of coupled products (Table I). Only moderate yields could be obtained with α-bromoacetate esters, even at higher reaction temperatures. Much shorter reaction



times were required when dibutyldiallyltin was used rather than tributylallyltin. The reaction with acetonyltin required higher temperatures than that with allyltin. Other organotin reagents such as tributylphenyltin, tributylvinyltin, tributyl(2-phenylethyl)tin, and tributylcyanomethyltin gave poor yields of coupled products (<10%) under all conditions studied.

The coupling reaction with α-iodo-γ-butyrolactone appeared to proceed primarily through a radical mechanism since both galvinoxyl and 1,4-cyclohexadiene completely stopped the 30 °C reaction with tributylallyltin while the 50 °C reaction with tributylacetonyltin was slightly supressed. In both cases, in the absence of the palladium catalyst, the reaction still proceeded to some extent. Similar results are also observed for the coupling of α-iodo-γ-butyrolactone with tributylacetonyltin. The coupling was slightly supressed in the presence of galvinoxyl but also took place in the absence of the palladium catalyst. The coupling of α-bromo-γ-butyrolactone with the acetonyltin reagent did not take place in the absence of the palladium catalyst, and it was not stopped by galvi-

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Table I. Coupling Reactions of Allyl- and Acetonyltin Reagents[a]

ester	X	allyltin reagent	conditions T, °C	conditions time, h	solvent	isolated yield, %
	I	n-$Bu_3SnCH_2CH{=}CH_2$	30	20	THF	97
				45		0[b,c]
				45		54[d]
		n-$Bu_2Sn(CH_2CH{=}CH_2)_2$	30	1	THF	87
	Br	n-$Bu_3SnCH_2CO{-}CH_3$	50	12	THF	73
						35[b]
						0[d]
	I		50	12	THF	82
						72[b]
						81[d]
XCH_2CO_2Et	Br	n-$Bu_3SnCH_2CH{=}CH_2$	50	18	THF	0
			100	13	$C_6H_5CH_3$	36
		n-$Bu_2Sn(CH_2CH{=}CH_2)_2$	90	24	$C_6H_5CH_3$	38
			100	6		67
		n-$Bu_3SnCH_2CO{-}CH_3$	100	9	$C_6H_5CH_3$	41
			50	48	THF	21

[a] Reactions were catalyzed with 1 mol % bis(triphenylphosphino)dichloropalladium(II) based on the halo ester. [b] 1 mol % galvinoxyl based on the halo ester was added. [c] The same result was obtained when 1 mol % of 1,4-cyclohexadiene based on the halo ester was added. [d] The palladium catalyst was omitted.

noxyl. Thus, it appears to proceed primarily via a palladium-catalyzed mechanism.

This coupling reaction with the acetonyltin reagent represents a much improved procedure for the synthesis of α-acetonyl-γ-butyrolactone,[7] which had previously been obtained by the thiazolium salt catalyzed addition of acetaldehyde to α-methylene-γ-butyrolactone.

Experimental Section

α-Acetonyl-γ-butyrolactone. To a dry Schlenk tube under nitrogen was added 35.1 mg (0.0501 mmol) of dichlorobis(triphenylphosphine)palladium(II), 0.825 g (5.00 mmol) of α-bromo-γ-butyrolactone, and 5.0 mL of dry tetrahydrofuran (distilled from sodium/benzophenone). After mixture was stirred for 15 min at 50 °C, 2.87 g (7.50 mmol) of acetonyltributyltin[9] was added to the yellow suspension. The resulting homogeneous yellow solution was stirred for 12 h at 50 °C and cooled to room temperature, and the solvent was removed under reduced pressure. The resulting oil was dissolved in 25 mL of acetonitrile and washed with hexane (3 × 10 mL). Removal of the acetonitrile gave an oil which was further purified by radial chromatography (chromatotron,[10] 50% ethyl acetate/hexane). Bulb-to-bulb distillation (64–70 °C (0.1 mmHg) [lit.[8] 102 °C (0.25 mm Hg)] yielded 0.515 g (73%) of α-acetonyl-γ-butyrolactone: ^1H NMR (270 MHz, $CDCl_3$) δ 1.86–2.02 (m, 2 H), 2.21 (s, 3 H), 2.48–2.59 (m, 2 H), 2.69 (dd, J = 8, 18 Hz, 1 H), 2.90–2.98 (m, 1 H), 3.08 (dd, J = 3, 18 Hz, 1 H), 4.23 (dt, J = 7, 10 Hz, 1 H), 4.40 (dt, J = 2, 9 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) 28.6, 29.7, 34.9, 43.5, 66.4, 178.5, 205.1; IR (neat) 1760, 1705 cm^{-1}; mass spectrum, m/z (relative intensity) 142 (M^+, 0.7).

The same procedure was used for the reaction of α-iodo-γ-butyrolactone.[11]

α-Allyl-γ-butyrolactone. A similar reaction procedure was employed for the coupling of tributylallyltin[12] with the α-halo-γ-butyrolactones. After partitioning between acetonitrile and hexane, the resulting oil was further purified by radial chromatography using (40% ethyl acetate/hexane). Bulb-to-bulb distillation (20 °C (0.025 mmHg) [lit.[13] bp 90 °C (7 mmHg)] gave the desired product:[13] ^1H NMR (270 MHz, $CDCl_3$) δ 1.87–2.12 (m, 1 H), 2.12–2.51 (m, 2 H), 2.51–2.78 (m, 2 H), 4.15–4.39 (m, 2 H), 5.07–5.21 (m,2 H), 5.68–5.92 (m, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) 27.7, 34.2, 38.7, 66.3, 117.4, 134.4, 178.4; IR (neat) 3078, 1766, 1641 cm^{-1}.

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Registry No. $Bu_3SnCH_2COCH_3$, 14583-98-3; $Bu_3SnCH_2CH{=}CH_2$, 24850-33-7; $Bu_3Sn(CH_2)_2Ph$, 14775-15-6; $Bu_3Sn(CH_2)CN$, 17729-59-8; $Ph(CH_2)_3CO_2Et$, 10031-93-3; $BrCH_2CO_2Et$, 105-36-2; $Bu_2Sn(CH_2CH{=}CH_2)_2$, 15336-98-8; $CH_2{=}CH(CH_2)_2CO_2Et$, 1968-40-7; $CH_3CO(CH_2)_2CO_2Et$, 539-88-8; Bu_3SnPh, 960-16-7; $Bu_3SnCH{=}CH_2$, 7486-35-3; $PhCH_2CO_2Et$, 101-97-3; $CH_2{=}CHCH_2CO_2Et$, 1617-18-1; $NC(CH_2)_2CO_2Et$, 10137-67-4; α-bromo-γ-butyrolactone, 5061-21-2; α-phenyl-γ-butyrolactone, 6836-98-2; galvinoxyl, 2370-18-5; 1,4-cyclohexadiene, 628-41-1; α-acetonyl-γ-butyrolactone, 71385-84-7; α-iodo-γ-butyrolactone, 31167-92-7; α-allyl-γ-butyrolactone, 10491-63-1; α-vinyl-γ-butyrolactone, 43142-60-5; α-(2-phenylethyl)-γ-butyrolactone, 3454-79-3; α-(cyanomethyl)-γ-butyrolactone, 932-48-9.

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Synthesis of Chrysene, 5-Substituted Chrysenes, and Chrysene Derivatives via Intramolecular Cycloaddition Reactions

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The chemistry of polynuclear aromatic hydrocarbons has been of continuing interest due to their widespread environmental distribution and the causal relationship between exposure and tumor production. An often-studied representative class of these compounds is the chrysene family. While chrysene is itself only weakly biologically active, 5-substituted chrysenes are much more potent in assays for mutagenic and carcinogenic activity.[1]

Several approaches to the synthesis of this class of compounds have been reported recently.[2] Our success

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