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2-Ethoxy-2-propenyl Diethyl Phosphate. An Efficient Halo Acetone Equivalent for the Pd-Catalyzed Cross-coupling with Tin Enolates

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In the presence of Pd(0) complexes, 2-ethoxy-2-propenyl diethyl phosphate was found to react with organotins to give the corresponding coupling products, showing to be a more efficient halo acetone equivalent compared with the corresponding acetate or carbonate. Reaction with tin enolates gave the 1,4-diketone in moderate to good yields.

In our earlier communication, the reaction of α-halo ketone bearing bulky groups with organotin enolates (mixtures of α-stannyl ketone and enol stannyl ether) has been reported to produce 1,4-diketones.1) However, the reaction of halo acetone with tin enolates gave the furan derivatives either in the presence or the absence of the palladium catalyst,2) showing that addition of the enolates to the carbonyl group of halo acetone was faster than the coupling process with the halo acetone. So the development of the halo acetone equivalent for the coupling reaction with organotins is desirable. In 1980, Trost et al. showed 2-ethoxy-2-propenyl acetate as an enolonium ion equivalent, but this was the less reactive substrate.3)

In this letter, we report that 2-ethoxy-2-propenyl diethyl phosphate was a more efficient substrate in place of halo acetone for the Pd-catalyzed reaction with organotins.

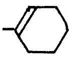
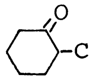
$$Bu_3SnR \; + \; CH_2{=}C(OEt)CH_2OPO(OEt)_2 \xrightarrow{[Pd]} \xrightarrow{H^+} R\text{-}CH_2COCH_3$$

2-Ethoxy-2-propenyl acetate, phosphate,4a) and carbonate4b) were prepared by the method reported for the acetate.3)

Table 1 shows the results of Pd-catalyzed reactions of 2-ethoxy-2-propenyl acetate, phosphate, and carbonate with several organotins, indicating that the phosphate gave the coupling products in the best yield, showing to be the most efficient halo acetone equivalent.

As Table 2 shows, Pd-catalyzed reaction of the phosphate with various tin enolates gave the 1,4-diketone regioselectively after hydrolysis in moderate to good yields.

Table 1. Pd-Catalyzed Reaction of Halo Acetone Equivalent with Organotins

$CH_2=C(OEt)CH_2$-X	Bu_3Sn-R[a)]	Product	GLC Yield/%[b)]
-OAc	-Ph	$PhCH_2C(OEt)=CH_2$	49
-OPO(OEt)$_2$			74
-OCO_2Me			17
-OAc	-C(OEt)=CH_2	$CH_2=C(OEt)CH_2C(OEt)=CH_2$	72
-OPO(OEt)$_2$			99
-OCO_2Me			63
-OAc	-O-	-$CH_2C(OEt)=CH_2$	(70)
-OPO(OEt)$_2$			(83)

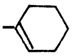
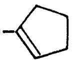
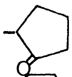
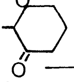
a) For R = Ph; 1 mol% of $Pd(PPh_3)_4$ in HMPA at 100 °C for 20 h. R = $C(OEt)=CH_2$; 0.5 mol% of $PdCl_2(PPh_3)_2$ in PhH at 100 °C for 20 h. R = O- ; 5 mol% of $Pd(PPh_3)_4$ in THF at room temperature for 4 h. b) In parenthesis, isolated yield.

Table 2. Pd-Catalyzed Reaction of the Phosphate with Tin Enolates

Tin enolate	Product (after hydrolysis)	Isolated yield/%
Bu_3Sn-CH_2COMe	$CH_3COCH_2CH_2COMe$	36
-$CH_2COCHMe_2$	$CH_3COCH_2CH_2COCHMe_2$	49
-$OCMe=CMe_2$	$CH_3COCH_2CMe_2COCMe$	61
-OEt=CHMe	$CH_3COCH_2CHMeCOEt$	68
-CH_2COPh	$CH_3COCH_2CH_2COPh$	68
-CHMeCOPh	$CH_3COCH_2CHMeCOPh$	71
-O-	CH_3COCH_2-	69
-O-	CH_3COCH_2-	83

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