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UNSYMMETRICAL MONOPROTECTED α-DIKETONES VIA THE PALLADIUM-CATALYZED VINYLATION OF ACID CHLORIDES WITH ORGANOTIN COMPOUNDS

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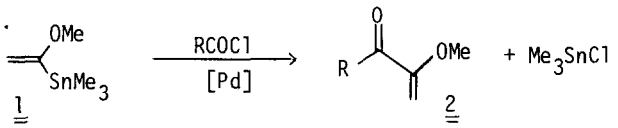
Abstract: Under benzyl(chloro)bis triphenylphosphinepalladium(II) catalysis, α-oxygenated vinyltin compounds undergo clean cross coupling with acid chlorides to give α-oxygenated enones which are converted to unsymmetrical α-diketones, butadienyl ethers or substituted methyl vinyl ketones.

We wish to report the efficient cross coupling of acid chlorides with (α-methoxyvinyl)trimethyltin[1] in refluxing benzene solution using 1 mol % benzyl(chloro) bis-triphenylphosphinepalladium(II) catalysis.



1 2

Table I. α-Methoxyenones

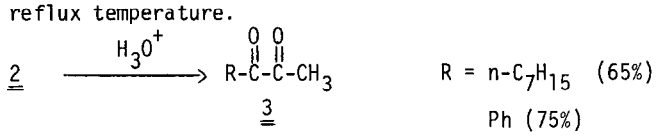
	R	Yield[a] (bp°C/mmHg)	Reaction Time[b](h)
2a	$-CH_3$	44 [77] (61-63/60)	1
2b	$-n-C_7H_{13}$	82 (60-61/0.15)	1
2c	$-c-C_6H_{11}$	86 (47-48/0.15)	1
2d	$-C(CH_3)_3$	79 [100](58-59/15	4
2e	$-(CH_2)_4Cl$	77 [95] (66/0.08)	1
2f	$-C_6H_5$	73 [100](83-85/0.6)	1
2g		83 (75-76/0.2)	1

[a]Isolated yield on 25 mmol reaction scale. Numbers in brackets represent gc yields using a hydrocarbon internal standard. [b]Reactions were carried out using an initial 1.0 M concentration of reactants.

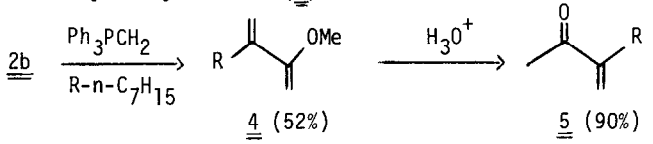
Recent studies have established that acid chlorides are coupled with organotin compounds using palladium catalysts to give the corresponding ketones.[3] For vinyl-and alkynyl-tri-n-butyltin, it was found that the unsaturated groups are transferred to the acid chloride preferentially. Our own studies on the preparation and reactions of organotin compounds containing a masked ketone functionality provided the ideal reagents to selectively assemble an unsymmetrical as well as monoprotected α-diketone in a single step.

The method is quite general for a variety of acid chlorides (cf Table I). Analysis of the reaction mixtures by gc reveals that clean formation of 2 and trimethyltin chloride occurs with the simultaneous disappearance of the starting materials. However, with continued heating, the yield of 2 diminishes regularly forming a polymeric material.

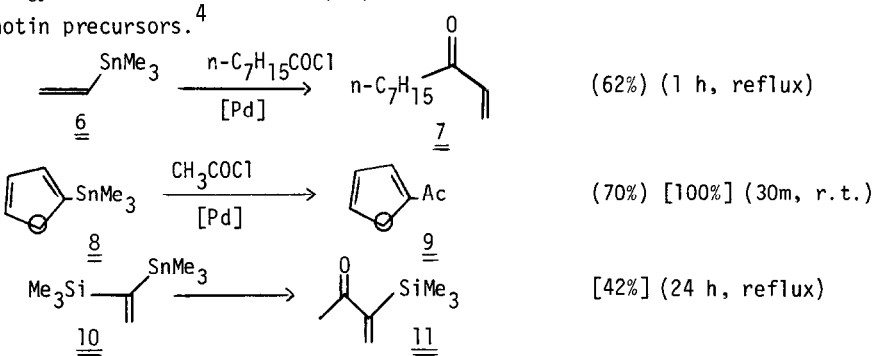
Hydrolysis of these α-methoxyenones (2) was accomplished using a 4:1 acetone - 1.0 M HCl mixture in 2.5h at reflux temperature.



For 2b, we also prepared the corresponding butadienyl compound (4) which was hydrolyzed to give a substituted methyl vinyl ketone (5).



This methodology is well suited to the preparation of other unsaturated ketones from the appropriate organotin precursors.[4]



Acknowledgement. We wish to thank the William and Flora Hewlett Foundation Grant of Research Corporation for financial support of this work.

References and Notes.

1. J.A. Soderquist and G. J-H Hsu, Organometallics, 1, 830 (1982). We find that addition of the α-methoxyvinyllithium solution to a cold (-78°) solution of trimethyltin chloride minimizes the formation of bis-α-methoxyvinyl(dimethyl)tin as a coproduct in the preparation of 1.

2. PMR, CMR, IR, MS, high resolution MS data consistent with the assigned structures were obtained for all new compounds.

3. (a) D. Milstein and J.K. Stille, J.Am.Chem.Soc., 100, 3636 (1978). (b) ibid., J.Org.Chem., 44, 1613 (1979). (c) M.W. Logue and K. Teng, J.Org.Chem., 47, 2549 (1982). (d) For a recent review of palladium-catalyzed cross-coupling reactions see: E-I. Negishi, Accts.Chem. Res., 15, 340 (1982). (e) For recent routes to symmetrical diketones from acid chlorides see: P. Girard, R. Couffignal and H.B. Kagan, Tetrahedron Lett., 22, 3959 (1981) and references therein.

4. The numbers in parentheses are isolated yields while those in brackets are gc yields. Vinyltin compounds were prepared from the reaction of Me_3SnCl and the corresponding vinyl Grignard reagent for 6 and 10 and α-lithiated furan for 8 (ca 80% yield in each case). For 11, a reaction by-product was observed.

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