

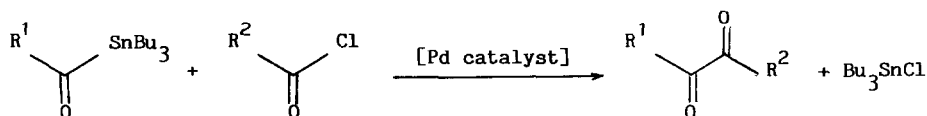
A VERSATILE ACCESS TO UNSYMMETRICAL AND SYMMETRICAL α -DIKETONES VIA ORGANOTIN REAGENTS

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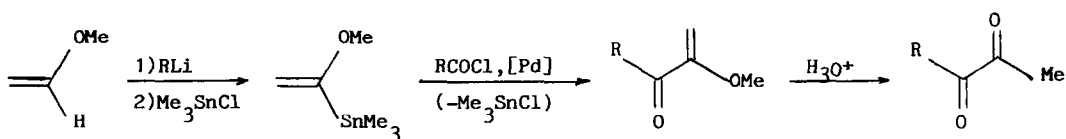
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ABSTRACT : Unsymmetrical α -diketones have been obtained via cross coupling of acyltins with acyl halides under $\text{PdCl}_2(\text{PPh}_3)_2$ catalysis while symmetrical α -diketones have been readily obtained via "in situ" formation of acyltins using hexabutylstannane and acyl chlorides under similar experimental conditions.

We wish to report an efficient access to unsymmetrical and symmetrical α -diketones via the cross coupling of acyltributyltins (1) with acyl chlorides under catalysis by palladium complexes :

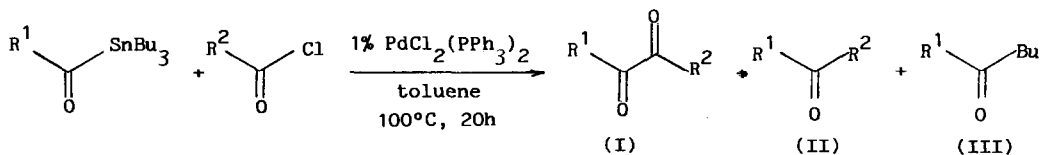


The synthesis of functional ketones via the cross-coupling of organotin derivatives with acyl halides has been extensively studied these last years (4-10), however, little attention has been devoted to the synthesis of α -diketones. Benzil was obtained in 35% yield in the reaction of N-phenyl,N-stannyl-imines with benzoyl chloride (11) and more interestingly, unsymmetrical monoprotected α -diketones and subsequently α -diketones were obtained in good yields by alkoxyvinylation of acyl chlorides (12) :



However, the clean preparation of the intermediate alkoxyvinyltin is connected with the presence of a single labile hydrogen meaning that the method is essentially valuable for the synthesis of α -diketones containing an acetyl moiety.

The cross coupling of acyltins with acyl chlorides performed in toluene in the presence of dichloro(bis-triphenylphosphine)palladium is more general and allows access to unsymmetrical (or symmetrical) α -diketones (I) accompanied by two side products : the decarbonylation product (II) and the product resulting from a butyl transfer (III).



The distribution of these three compounds and the isolated yields of α -diketones after liquid chromatography are given in table I.

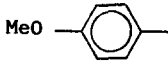
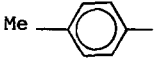
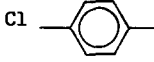

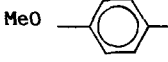
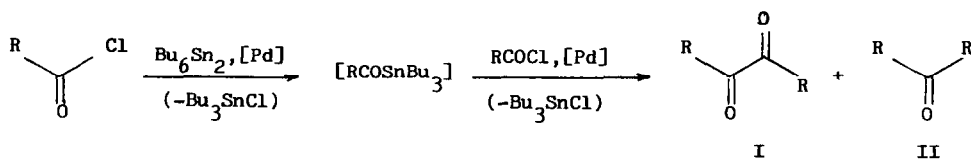
R^1 -C(=O)-SnBu ₃	R^2 -C(=O)-Cl	Products distribution			R^1 -C(=O)-C(=O)-R ² (yields) ^(b)
		I	II	III	
$R^1 = i\text{-Pr}$	$R^2 = \text{Ph}$	93	4	3	59%
$i\text{-Pr}$		95	3	2	65%
$i\text{-Pr}$		92	6	2	63%
$i\text{-Pr}$		78	16	6	53%
$i\text{-Pr}$		84	11	4	54%
Et		93	2	5	61%
Et	Hex	75	20	5	41%

Table I : Synthesis of unsymmetrical α -diketones via cross-coupling of acyltins with acyl chlorides ^(a)

- a) Acyltin (11 mmoles) and acyl chloride (10 mmoles) were heated at 100°C in toluene (15 ml) in the presence of PdCl₂(PPh₃)₂ (0.1 mmole) under nitrogen (sealed tube) for about 20h, until the appearance of a black precipitate.
- b) Isolated yields after elimination of Bu₃SnCl as Bu₃SnF precipitate (19) and liquid chromatography on silicagel (solvent : 95/5 pentane/ether mixture)(20).

In the case of the synthesis of symmetrical α -diketones, an interesting alternative is the "in situ" generation of the acyltin upon reaction of the acyl halide with hexabutyliditin in the presence of dichloro(bis-triphenylphosphine) palladium :



This type of reaction has been very recently disclosed by BELETSKAYA and coworkers with hexaethylditin used under a carbon monoxide pressure (13). However, the use of hexabutylditin, much less toxic and commercially available constitutes a remarkable improvement because the decarbonylation is much more limited, allowing access to symmetrical α -diketones in reasonable yields without use of carbon monoxide. Furthermore when the reactions are performed under carbon monoxide (15 atm) the decarbonylation is almost avoided (cf. Table II).

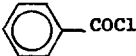
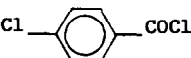
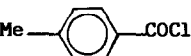

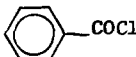
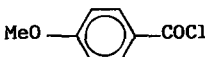
Entry	RCOCl	Products distribution ^(c)		R-C-C-R ^(d) O O
		I	II	
1(a)		85	15	52%
2(a)		73	27	45%
3(a)		83	17	55%
4(a)		88	12	63%
5(b)		98	2	65%
6(b)		98	2	58%

Table II : Synthesis of symmetrical α -diketones via reaction of hexabutylditin with acyl chlorides

a) Hexabutylditin (11 mmoles) and acyl chloride (20 mmoles) were heated in toluene (15 ml) at 110°C in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ (0.14 mmole) under nitrogen (sealed tube) for a period of 24 hours.

b) These reactions were performed under a carbon monoxide pressure of 15 atm.

c) The amount of RCOBu can be neglected ($\sim 1\%$)

d) Isolated yields after elimination of Bu_3SnCl (as Bu_3SnF precipitate) and liquid chromatography on silicagel (20).

This synthesis of α -diketones cannot really be compared with conventional preparations like oxidation of acyloins, α -methylene ketones or acetylenic compounds (14) where the desired skeleton is initially contained in the molecule, but it appears

competitive with methods involving coupling of acyl halides in the presence of samarium diiodide (15) or carbonylation of organometallic reagents (16-18) in terms of generality or ease of the workup.

More detailed studies in view of extensions and improvements of these synthetic methods are in progress.

ACKNOWLEDGEMENTS

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- 20) The α -diketones were unambiguously identified on the basis of their physicochemical data (IR, NMR, UV, MS) and their purities were subsequently checked using gas-chromatography.

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