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'ALK-1-YNYLLEAD TRIACETATES' AS ALK-1-YNYL CARBOCATION EQUIVALENTS.
THE α-ALK-1-YNYLATION OF β-DICARBONYL COMPOUNDS AND NITRONATE SALTS

Mark G. Moloney, John T. Pinhey* and Eric G. Roche

Department of Organic Chemistry, University of Sydney, Sydney 2006, Australia

Summary: The addition of lead tetraacetate to a chloroform solution of alk-1-ynyltrimethylstannane results in the rapid formation of trimethylstannyl acetate and an unstable species, believed to be the corresponding alk-1-ynyllead triacetate, which can effect the rapid α-alkynylation of β-dicarbonyl compounds and nitronate salts.

Nucleophilic substitution at acetylenic carbon is an area of considerable interest, both from its usefulness in synthesis and from mechanistic considerations.[1,2] Although a variety of reactions of this type have been developed, substitution by enolate anions to give α-ethynyl ketones and esters has only recently been reported by Kende.[3]

We now report that the addition of a chloroform solution of ethyl 2-oxocyclopentanecarboxylate (1) (1.0 equiv.) to the mixture produced on reacting phenylethynyltrimethylstannane (2a) (1.1 equiv.) in chloroform at room temperature with lead tetraacetate (1.0 equiv.) results in the rapid formation of the α-phenylethynyl β-keto ester (3a). The yield of (3a) was found to be dependent on the time between the mixing of the stannane (2a) with lead tetraacetate, and the addition of the β-keto ester (1); it was a maximum (73% isolated yield) when this was 0.5 min. If the addition of (1) was made 10 min after mixing the tin and lead reagents the yield of (3a) was 25%, while a further reduction to 8% resulted when this period was increased to 0.5 h. Thus the alkynylation reaction would appear to involve an unstable species, which we believe to be phenylethynyllead triacetate (4), produced in a metal-metal exchange reaction indicated in Scheme 1. Analogous tin-lead exchange reactions occur in the case of arylstannanes[4] and alk-1-enylstannanes,[5,6] while there are precedents for the alkynylation reaction in the α-arylation[7] and α-vinylation[6] of β-dicarbonyl compounds by aryllead triacetates and vinyllead triacetates respectively.

Evidence for the above proposal is to be found in the formation of trimethylstannyl acetate in quantitative yield (n.m.r. spectroscopic determination) 0.5 min after mixing the stannane (2a) and lead tetraacetate in deuterochloroform. Further, when a mixture of (2a) and lead

Table 1. Reactions of alk-1-ynylstannane/LTA mixtures with β-dicarbonyl compounds and nitronate salts.[a]

Entry	Stannane	Solvent	Nucleophile	Product	Isolated Yield(%)
1	(2a)	$CHCl_3$	(1)	(3a)	73(78)[b]
2	(2a)	$CHCl_3$	(6)	(10a)	87
3	(2a)	DMSO	(7)	(11)	58
4	(2a)	DMSO	(8)	(12a)	72
5	(2a)	DMSO	(9)	(13a)	62
6	(2b)	$CHCl_3$	(1)	(3b)	54(77)[b]
7	(2b)	$CHCl_3$	(6)	(10b)	75
8	(2b)	DMSO	(8)	(12b)	47
9	(2b)	DMSO	(9)	(13b)	53
10	(2c)	$CHCl_3$	(1)	(3c)	57
11	(2c)	$CHCl_3$	(6)	(10c)	69
12	(2c)	DMSO	(9)	(13c)	48
13	(2d)	$CHCl_3$	(1)	(3d)	78
14	(2d)	$CHCl_3$	(6)	(10d)	77(82)[c]
15	(2d)	$CHCl_3$	(9)	(13d)	60

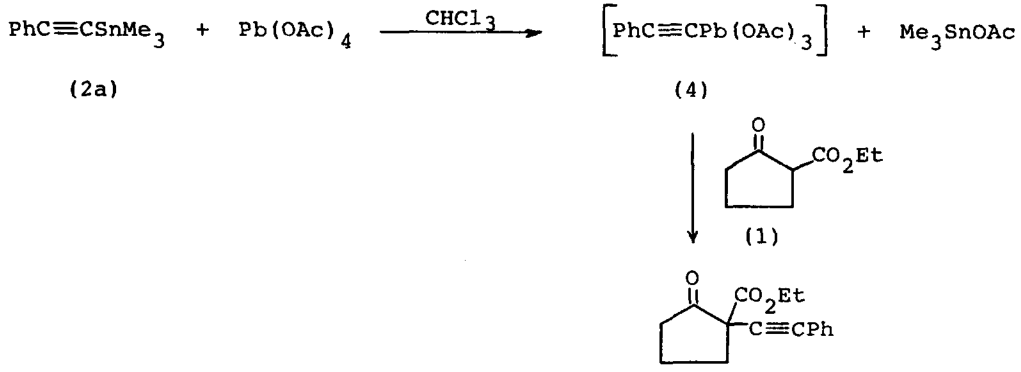
[a] Reactions were performed as indicated in the text for the synthesis of the phenylethynyl derivative (3a), unless otherwise specified. The substrate concentration was 0.2-0.3M. For entries 1-12, the substrate was added 0.5 min after mixing the stannane and LTA, while for entries 13-15 the time was increased to 20 min. Reactions were complete within 10 min of addition of substrate, and were worked up after 0.5-1.0 h. All new compounds gave the expected microanalytical and spectroscopic data.

[b] 2.2 equiv. of (2a) and 2.0 equiv. of LTA used.

[c] 1.5 equiv. of (2d) and 1.1 equiv. of LTA used.

tetraacetate is kept in chloroform for 3 h, the only isolable product (46%) is tetraphenylethynyllead (5), which does not react with the β-keto ester (1). An attempt to isolate the proposed intermediate (4) by precipitation with a cold dry light petroleum/ether (1:1) mixture gave an unstable solid which, when added immediately to a chloroform solution of the keto ester (1), gave the α-phenylethynyl derivative (3a) in 19% yield.

In an initial examination of the scope of this alkynylation reaction, the stannanes (2a)-(2d), the dicarbonyl compounds (1), (6), and (7), and nitronate salts (8) and (9) have been investigated. Yields (see Table 1) were generally moderate to good, and the results would indicate that the method should be applicable to a wide range of monosubstituted acetylenes,

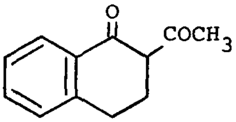


Scheme 1

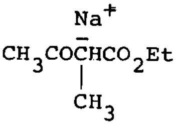
(3a)

$(PhC\equiv C)_4Pb$

(5)

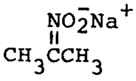


(6)



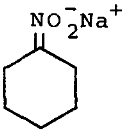
$CH_3CO\underset{|\,CH_3}{\overset{Na^+}{\bar{C}}}HCO_2Et$

(7)



$CH_3\overset{NO_2^-Na^+}{\overset{\|}{C}}CH_3$

(8)



(9)

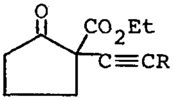
$RC\equiv CSnMe_3$

(2a) R = Ph

(2b) R = $CH_3(CH_2)_5$

(2c) R = H

(2d) R = Me_3Si

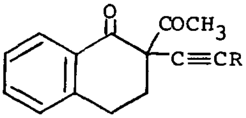


(3a) R = Ph

(3b) R = $CH_3(CH_2)_5$

(3c) R = H

(3d) R = Me_3Si

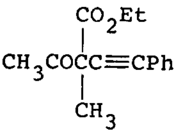


(10a) R = Ph

(10b) R = $CH_3(CH_2)_5$

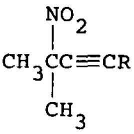
(10c) R = H

(10d) R = Me_3Si



$CH_3CO\underset{CH_3}{\overset{CO_2Et}{C}}C\equiv CPh$

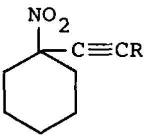
(11)



$CH_3\underset{CH_3}{\overset{NO_2}{C}}C\equiv CR$

(12a) R = Ph

(12b) R = $CH_3(CH_2)_5$



(13a) R = Ph

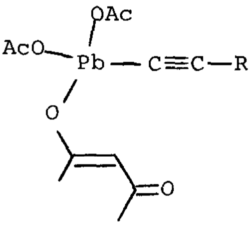
(13b) R = $CH_3(CH_2)_5$

(13c) R = H

(13d) R = Me_3Si

β-dicarbonyl compounds, and nitronate salts. In all cases the alkynyllead(IV) intermediate showed similar instability to that of the phenylethynyl derivative (4), and thus the yield may be improved by the use of excess reagent. This has been demonstrated for the keto esters (3a) and (3b), and diketone (10d) (entries 1, 6, and 14 respectively).

In the above reactions, the alkynyllead intermediate is behaving as an alk-1-ynyl cation equivalent; however the mechanism of the reaction remains obscure. A nucleophilic addition-elimination sequence would appear most unlikely since the acetylenes (2b) and (2c) do not have a group on the β carbon to stabilise a negative charge. Kende[3] found that enolates react readily with 1-chloro-2-phenylethyne by such a mechanism, but fail to react with 1-chloro-1-hexyne. In view of the nature of the substrates which undergo our reaction, it would appear quite possible that an initial step involves ligand exchange to give, in the case of a dicarbonyl compound, a lead(IV) intermediate of the type shown in structure (14).



(14)

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