α-Alkenylation of β-Dicarbonyl Compounds with 'Alk-1-enyl-lead Triacetates'

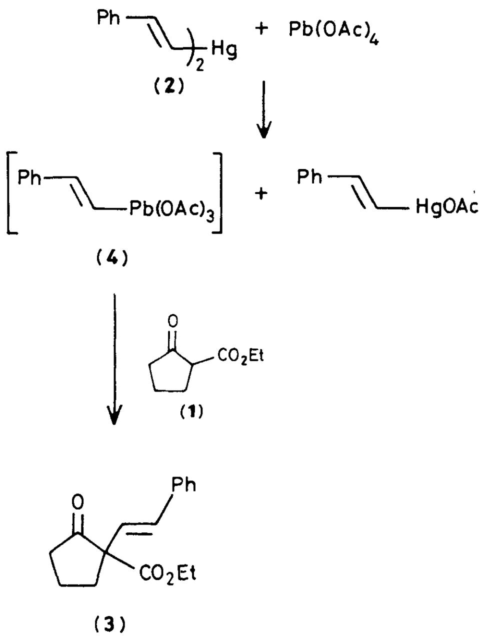
Mark G. Moloney and John T. Pinhey*

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

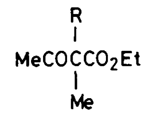
Addition of lead tetra-acetate to a chloroform solution of a dialk-1-enylmercury or an alk-1-enyltributylstannane results in rapid formation of a relatively unstable species, believed to be an alk-1-enyl-lead triacetate, which can be used for the α-alkenylation of β-dicarbonyl compounds.

The introduction of alk-1-enyl groups α to a carbonyl group has received much attention in recent years, owing to the development of routes to biologically important compounds, and to the search for new synthetic methods. The present methods depend mainly on the introduction of a unit (*e.g.* by S_N reaction, Michael addition, or addition to carbonyl) containing a group from which a β,γ-double bond can subsequently be generated.[1,2] However, there have been two reports of the direct introduction of alkenyl groups. These involve the reaction of an ester enolate[3] or a Reformatsky reagent[4] with a vinyl halide in the presence of a nickel catalyst.

We now report that the addition of the β-keto ester (**1**) to a mixture of (*E*,*E*)-distyrylmercury (**2**) and lead tetra-acetate in chloroform–pyridine leads to the formation of the β,γ-unsaturated β-keto ester (**3**)† in 65% yield. We believe that

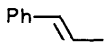


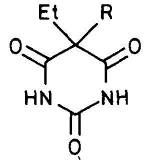
Scheme 1



$$\begin{array}{c} R \\ | \\ \mathrm{MeCOCCO_2Et} \\ | \\ \mathrm{Me} \end{array}$$

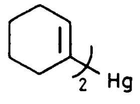
(**5**) R = H

(**7**) R = 

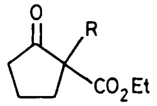


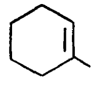
(**6**) R = H

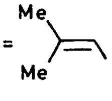
(**8**) R = 

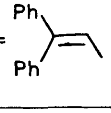


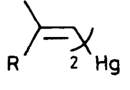
(**9**)



(**12**) R = 

(**13**) R = 

(**14**) R = 



(**10**) R = Me

(**11**) R = Ph

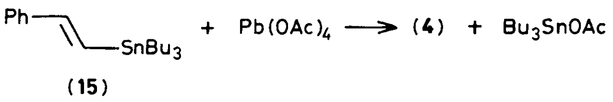
---

† All new compounds were characterised fully by microanalytical and spectroscopic methods.

the reactive species is (*E*)-styryl-lead triacetate (**4**), produced in a metal–metal exchange reaction indicated in Scheme 1. There is ample precedence for the mercury–lead exchange[5] and (*E*)-styrylmercury acetate has been shown to be produced in the reaction, while there is an analogy for the vinylation reaction in the arylation of β-dicarbonyl compounds by aryl-lead triacetates.[6] Isolation of the lead compound (**4**) has yet to be achieved; however, the n.m.r. spectroscopic data are consistent with the formation of such a species, which in the absence of (**1**) decomposes to (*E*)-styryl acetate and lead(II) acetate.

A preliminary investigation of the scope of this vinylation reaction has indicated that it could be widely applicable. Replacement of the keto ester (**1**) in the above reaction (Scheme 1) by ethyl methylacetoacetate (**5**) and 5-ethylbarbituric acid (**6**) led to the formation of the α-styryl derivatives (**7**) and (**8**) in yields of 52 and 66%, respectively. We have also shown that other dialk-1-enylmercury compounds can replace (**2**) in Scheme 1; thus, with dicyclohex-1-enylmercury (**9**), bis(2-methylprop-1-enyl)mercury (**10**), and bis(2,2-diphenylvinyl)mercury (**11**) the α-substituted β-keto esters (**12**), (**13**), and (**14**) were produced in yields of 80, 60, and 59%, respectively.

The synthesis of the (*E*)-styryl derivative (**3**) can also be achieved by adding ethyl 2-oxocyclopentanecarboxylate (**1**) to a mixture of (*E*)-styryltributylstannane (**15**) and lead tetra-acetate in chloroform. The yield of (**3**) is similar to that obtained with the mercury compound (**2**), and we believe that the same organolead intermediate (**4**) is the reactive species, being formed as indicated in Scheme 2.‡ The n.m.r. spectral data support this proposal and tributylstannyl acetate is a product of the reaction. Although only two other derivatives, (**7**) and (**8**), have been prepared by the stannane route, it may well be more useful than the mercury route because of the greater stability of the lead intermediate (**4**) when prepared in this way. Of particular interest in this regard is the difference in the products of decomposition of the lead intermediate in the two reactions, in the absence of a β-dicarbonyl compound. In the case of the stannane (**15**), there is a slow formation of phenylacetylene, which is the expected product from the work of Corey,[7] while, as noted above, (*E*)-styryl acetate is produced from the mercury compound (**2**). The latter result is thought to be due to involvement of a mercury compound and we hope to resolve this point with the isolation of an alk-1-enyl-lead triacetate.



Scheme 2

This work was supported by a grant from the Australian Research Grants Scheme.

Received, 9th April 1984; Com. 498

References

1 T. C. T. Chang and M. Rosenblum, *Tetrahedron Lett.*, 1983, **24**, 695, and references therein.

2 P. F. Hudrlik and A. K. Kulkarni, *J. Am. Chem. Soc.*, 1981, **103**, 6251, and references therein.

3 A. A. Millard and M. W. Lathke, *J. Am. Chem. Soc.*, 1977, **99**, 4833.

4 J. F. Fauvarque and A. Jutland, *J. Organomet. Chem.*, 1979, **177**, 273.

5 R. P. Kozyrod and J. T. Pinhey, *Tetrahedron Lett.*, 1982, **23**, 5365.

6 J. T. Pinhey and B. A. Rowe, *Aust. J. Chem.*, 1980, **33**, 113.

7 E. J. Corey and R. H. Wollenberg, *J. Am. Chem. Soc.*, 1974, **96**, 5581.

---

‡ Vinyl-lead triacetates have also been proposed by Corey[7] as unstable intermediates in the formation of acetylenes on treatment of alk-1-enyltributylstannanes with lead tetra-acetate in acetonitrile.