Trimethylstannylethylidenetriphenylphosphorane. A New Reagent for Organic Synthesis

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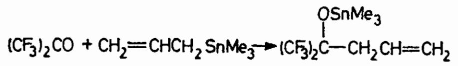
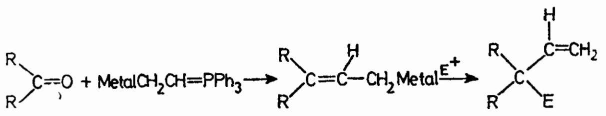
Summary A new type of metalloalkyl ylide has been produced which can be used to convert a ketone or aldehyde function directly to a very nucleophilic double bond; this affords a method for preparing quaternary carbons either by ring closure or external electrophilic reaction.

SIMPLE, regiospecific reactions of electrophiles with aryl or allylmetal compounds, [equation (1)], rationalized in terms of the strong resonance (+*I*) effects shown for $-CH_2$metal groups, prompted us to seek convenient methods of preparing β-metalloalkyl olefins. Attachment of the $=CHCH_2$-metal functionality directly to carbon compounds through the Wittig reaction offers a simple and versatile approach [equation (2)].

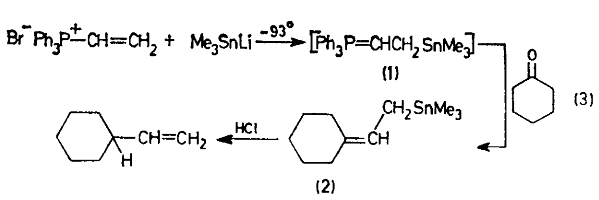
The addition of trimethyltinlithium in tetrahydrofuran[3] to vinyltriphenylphosphonium bromide[4] in ether at −93° over 10 min with a further 5 min at −93° gave the red ylide (**1**). This could be titrated at −93° with cyclohexanone to the disappearance of the red colour. After slowly warming to room temperature, filtering, and washing



$$(CF_3)_2CO + CH_2{=}CHCH_2SnMe_3 \rightarrow (CF_3)_2\overset{\overset{\displaystyle OSnMe_3}{|}}{C}{-}CH_2CH{=}CH_2 \qquad (1)$$



(2)



the ethereal solution with water an almost quantitative yield of the tin compound (**2**)† was obtained. The identity of compound (**1**) was established by isolating it in rather low yield by distillation[4a] or, alternatively, the crude reaction mixture, after warming to room temperature, was hydrolysed with aqueous hydrochloric acid (enough to make the mixture 1·0 M in HCl) for about 10 h at room temperature to cleave the tin compound.[2f] This method afforded a 90% yield (by g.l.c. analysis) of vinylcyclohexane‡ based upon cyclohexanone.

This reaction is, in principle, applicable to electrophiles other than HCl[1e] and metal nucleophiles other than R_3Sn-Li,[2a–e] and should afford a general method for either ring closure[5] or external electrophilic attack to yield vinyl quaternary carbon centres.[6]

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† The n.m.r. and mass spectra of this compound are in agreement with the proposed structure.

‡ Identified by comparison of the n.m.r. and g.l.c. behaviour with those of an authentic sample (Aldrich). Similar results, with somewhat lower yields, were obtained using acetone or acetaldehyde instead of cyclohexanone.

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[6] The substitution of other metal anions such as cyclopentadienylirondicarbonyl sodium for trimethyltinlithium should also offer a convenient entry into the synthetic chemistry described by Rosenblum *et al.*; A. Rosen, M. Rosenblum, and J. Tancrede, *J. Amer. Chem. Soc.*, 1975, **95**, 3062, and references therein.