Radical Reactions in Synthesis: Carbon–Carbon Bond Formation from 2-Substituted Allyl Trialkyl Stannanes

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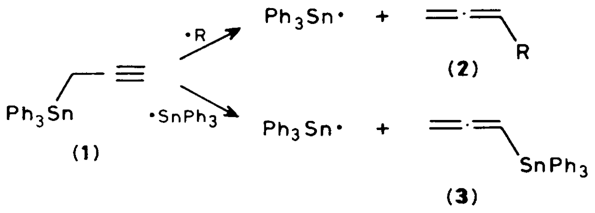
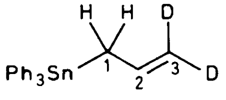
A competing 1,3-rearrangement of allyl stannanes has been demonstrated to occur under the normal thermal homolytic allyl transfer reaction conditions which limits the substitution patterns in these processes; two methacrylyl stannanes are described which allow the transfer of the methacrylyl moiety to alkyl bromides and iodides under mild conditions.

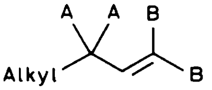
In the course of our investigation of the allene transfer process, *via* S_H2' reaction on prop-2-ynyl stannanes, *e.g.* (**1**), with alkyl radicals to yield allenes (**2**) we found that for good preparative yields an excess of stannane (**1**) was required.[1] This arose from a competing S_H2' reaction of the stannyl radical with the acetylene (**1**) to give the unreactive 1,2-dienylstannane (**3**) (Scheme 1). As allyl stannanes have been used for allyl transfers[2] we have investigated the possibility that a similar competition occurs in these cases. Thus, 3,3-dideuterioallyl(triphenyl)stannane (**4**) {from triphenylstannyl-lithium and [3,3-$^2H_2$]allyltoluene-4-sulphonate in tetrahydrofuran (THF) at −20 °C} was treated with alkyl halides under thermal conditions [alkyl halide (1 equiv.), (**4**) (2 equiv.), azobisisobutyronitrile (AIBN) (20 mol%), benzene, reflux, 12—36 h] to give the allyl alkanes (**5**). The results (Table 1) show that as the reactivity of the alkyl halide decreased from tertiary bromide to primary chloride then also the degree of allyl rearrangement in the product (**5**) increased. Control experiments showed that the allyl products (**5**) were stable to the reaction conditions whereas the stannane (**4**) in refluxing benzene and AIBN (20 mol%, 12 h) was completely scrambled, presumably by way of an S_H2' process involving the triphenylstannyl radical. Clearly this rearrangement, which occurs in both alkynyl- and allyl-stannanes, puts severe restraints on the location of substituents on the C-3 fragment, and in the allyl series implies that the 2-substituent will be most satisfactory, as the competing rearrangement is degenerate. In this connection it has been observed that 2-methylallyl-tri-n-butylstannane[3a] is an efficient reagent, whereas the 3-methyl isomer is not (allyl transfer yields <5%).[3b] However



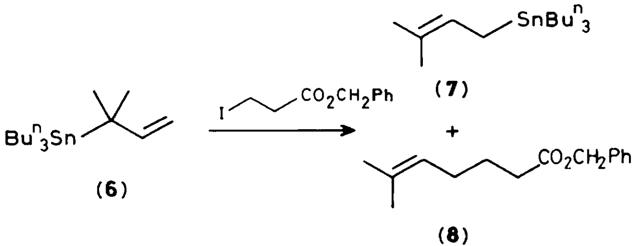
Scheme 1

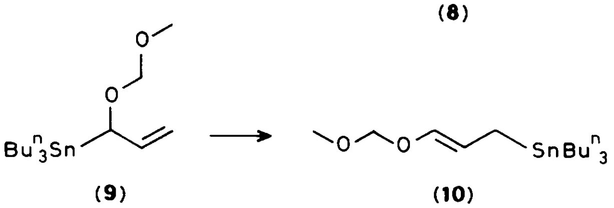


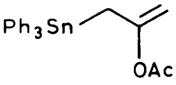
(**4**)



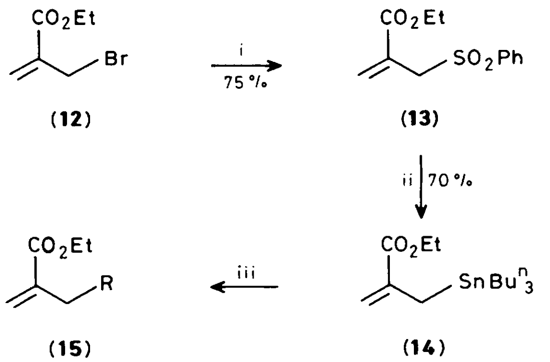
(**5**) **a**; A = D, B = H
b; A = H, B = D



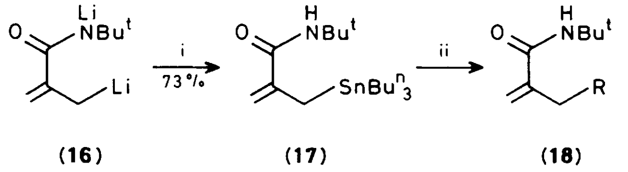




(**11**)



Scheme 2. *Reagents:* i, $NaSO_2Ph$ (2 equiv.), MeOH, reflux, 12 h; ii, $Bu^n{}_3SnH$ (2 equiv.), AIBN (cat.), benzene, 80 °C, 1.5 h (*cf.* ref. 6); iii, alkyl halide RX, (**14**) (2 equiv.), AIBN (cat.), benzene, 80 °C, 2—15 h.



Scheme 3. *Reagents:* i, tetramethylethylenediamine, hexamethylphosphoric triamide, $Bu^n{}_3SnCl$ (1 equiv.), −20→ +25 °C, then H_2O; ii, alkyl halide RX, (**17**) (2 equiv.), AIBN (cat.), benzene, reflux, 2—15 h.

Table 1. Reaction of alkyl halides with (**4**).

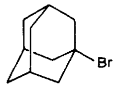
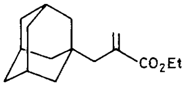
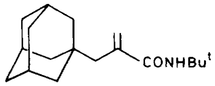
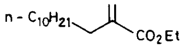
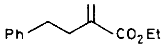
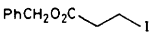
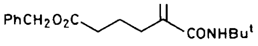
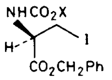
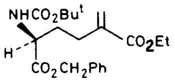
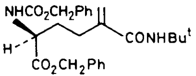
Alkyl halide	Reaction time/h	Product ratio (**5a**) : (**5b**) yield (%)
1-Bromoadamantane	12	>10 : 1, 88%
1-Iododecane	12	>10 : 1, 45%
1-Bromodecane	24	75 : 25, 16%
1-Chlorodecane	36	50 : 50, 4%

the electronic nature of the 2-substituent, as well as substitution at C-1, seems largely unexplored.†

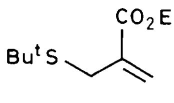
Substitution at C-1 was not satisfactory. Thus the stannane (**6**),[4] under thermal conditions (toluene, reflux, 48 h, cat. AIBN), gave rearranged stannane (**7**) (48%) and <5% of (**8**) with 3-iodobenzyl propionate. Similarly the 1-alkoxyallyl stannane (**9**)[5] gave only the rearranged 3-alkoxyallyl stannane (**10**) with a series of allyl halides and again this rearrangement was found to be catalysed by AIBN, in the absence of allyl halides.

In contrast substitution at C-2 provided a useful reagent when the substituent was electron withdrawing. Thus, whereas the enol acetate (**11**)[6] gave no useful transfers (thermal, AIBN conditions), the acrylate (**14**), [prepared from (**12**),[7] (Scheme 2)], and the acrylamide (**17**) [prepared from dilithio derivative (**16**)[8] and triphenylstannyl chloride (Scheme 3)] both gave efficient transfers of the methacrylyl moiety to alkyl halides under the usual thermal conditions (Table 2). Recently it was reported[9] that the 2-substituted allyl sulphides (**19**) and (**20**) undergo similar transfer reactions; however in comparison to (**19**) the reagent (**14**) described herein required significantly lower reaction temperatures (80 *vs.* 132 °C), which may be of significance in examples of sensitive substrates.

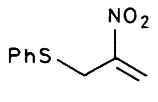
Table 2. Reaction of alkyl halides with (**14**) and (**17**).

Alkyl halide RX	Product (**15**) from (**14**) (%)	Product (**18**) from (**17**) (%)
	 70%	 76%
n-$C_{10}H_{21}I$	 70%	—
$PhCH_2Br$	 76%	—
	—	 62%
	 70%[a]	 62%[b]

[a] X = Bu^t. [b] X = $PhCH_2$.



(19)



(20)

In summary we have disclosed here new reagents for the direct transfer of the methacryl moiety to alkyl halides, which proceeds under mild conditions.

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† Keck[3b] has reported that a 6 : 4 mixture of 3-methylallyl- and 1-methylallyl-tri-n-butylstannanes gave, with a secondary bromide, a 1 : 1 mixture of products of reduction (replacement of bromide by hydrogen) and 3-methylallyl transfer (66% overall yield) under conditions in which the 3-methylallyl tri-n-butylstannane did not react (toluene, 80 °C, AIBN, 8 h, excess of stannanes as reagents).