Allene Transfer Reactions. A New Synthesis of Terminal Allenes

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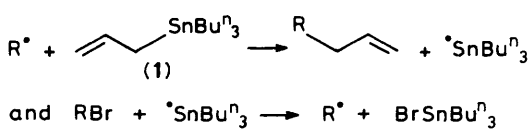
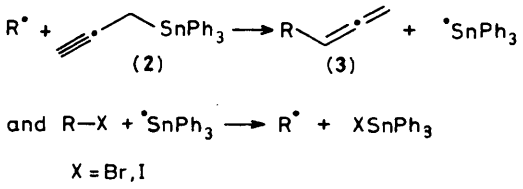
Alkyl radicals, produced from alkyl bromides and iodides, react smoothly with triphenylprop-2-ynylstannane to provide terminal allenes; this new reaction has been applied to a simple and stereospecific synthesis of the naturally occurring allenic amino-acid, *S*-2-aminohexa-4,5-dienoic acid.

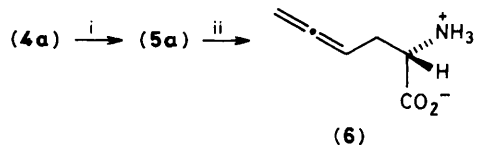
Recently the application of radical reactions in organic synthesis has become an area of interest.[1] The 'allyl transfer' reaction from allyltri-n-butylstannane (**1**) originally discovered by Pereyre[2] and Migita[3] and then subsequently exploited by Keck[4] is a valuable synthetic method (Scheme 1). We have now discovered that triphenylprop-2-ynylstannane[5]



Scheme 1

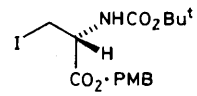
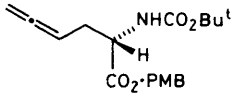
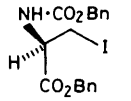
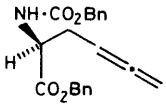
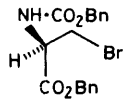
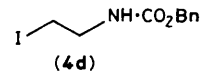
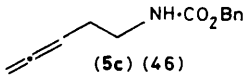
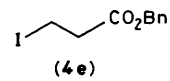
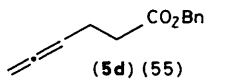
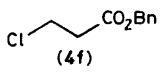
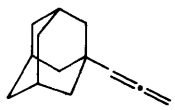


Scheme 2



Scheme 3. *Reagents:* i, (**2**) (4 equiv.), C_6H_6, reflux, AIBN (0.15 equiv.), 24 h; ii, TFA, anisole, 30 min, 20 °C.

Table 1.[a,b]

Entry	Substrate	Product (%)
1	 (**4a**)	 (**5a**) (55)
2	 (**4b**)	 (**5b**) (60)
3	 (**4c**)	(**5b**) (55)
4	 (**4d**)	 (**5c**) (46)
5	 (**4e**)	 (**5d**) (55)
6	 (**4f**)	(**5d**) (<5)
7	1-Bromoadamantane (**4g**)	 (**5e**) (45)

[a] PMB = 4-methoxybenzyl. [b] Bn = benzyl.

(**2**) provides 'allene transfer' to suitable alkyl bromides and iodides to form compounds (**3**) (Scheme 2).

The scope of this reaction is illustrated in Table 1, which records the results of treating substrates (**4a—g**) with triphenylprop-2-ynylstannane (**2**) (4 equiv.)† at reflux in degassed benzene under nitrogen (24 h),‡ to provide the allenes (**5a—e**).§

† An excess of triphenylprop-2-ynylstannane is required as this reagent isomerises to the more stable triphenylprop-1,2-dienylstannane under the reaction conditions, see M. Lequan and G. Guillerm, *C. R. Acad. Sci., Ser. C*, 1969, **268**, 858.

‡ Azobis(isobutyronitrile) (AIBN) (0.15 equiv.) was added ($T = 0$) to initiate the reaction.

§ All new compounds were fully characterised by analytical and spectral data.

The procedure appears to be compatible with most standard protecting groups and good to reasonable yields were obtained for alkyl iodides and bromides. As an illustration of the use of this reaction we have carried out a relatively simple and stereodefined synthesis of the unusual naturally occurring amino-acid (**6**), *S*-2-aminohexa-4,5-dienoic acid.[6] Thus (**5a**), after deprotection [trifluoroacetic acid (TFA), anisole, 30 min, 20 °C, 82%] and purification (h.p.l.c., reverse phase ODS column), gave *S*-2-aminohexa-4,5-dienoic acid (**6**) [45% from (**4a**)], δ_H (300 MHz, ^2H_2O) 2.36—2.45 (2H, m, 3-CH_2), 3.63 (1H, dd, *J* 4.8, 6.9 Hz, 2-CH), 4.66 (2H, m, obscured, 6-CH_2), and 4.90—5.00 (1H, m, 4-CH), δ_C (62.9 MHz, ^2H_2O) 29.87 (t, 3-C), 54.09 (d, 2-C), 75.77 (t, 6-C), 83.59 (d, 4-C), 174.04 (s, 1-C), and 209.27 (s, 5-C), ν_{max} (KBr) 1955m (C=C=C), 1580s (CO_2^-), and 842m cm^{-1} (CH_2=), *m/z* MH^+ (desorption chemical ionisation) 128, (Scheme 3).

That no loss of stereochemistry[1a] has occurred was shown by reduction of (**6**)¶ to 2-*S*-norleucine, $[\alpha]_D^{20}$ + 22.6° (*c* 0.3 in 5 M HCl) [lit.,[7] +23.5° (*c* 4 in 6 M HCl)].

Received, 5th July 1984; Com. 959

References

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2 J. Grignon and M. Pereyre, *J. Organomet. Chem.*, 1973, **61**, C33; J. Grignon, C. Servens, and M. Pereyre, *ibid.*, 1975, **96**, 225.

3 M. Kosugi, M. Kurino, K. Takayama, and T. Migita, *J. Organomet. Chem.*, 1973, **56**, C11.

4 G. E. Keck, E. J. Enholm, and D. F. Kachensky, *Tetrahedron Lett.*, 1984, **25**, 1867; G. E. Keck and J. B. Yates, *J. Organomet. Chem.*, 1983, **248**, C21; *J. Am. Chem. Soc.*, 1982, **104**, 5829; *J. Org. Chem.*, 1982, **47**, 3591.

5 M. Lequan and P. Cadiot, *C. R. Acad. Sci., Ser. C*, 1962, **254**, 133.

6 This amino acid (**6**), isolated from a mushroom *Amanita solitaria* (W. S. Chilton, G. Tsou, L. Kirk, and R. G. Benedict, *Tetrahedron Lett.*, 1968, **60**, 6283) was previously synthesised from diethyl formylaminomalonate and 4-bromobuta-1,2-diene (80%) and subsequent basic hydrolysis (35%) in *racemic* form in 28% overall yield by D. K. Black and S. R. Landor, *J. Chem. Soc. C*, 1968, 283.

7 W. A. Hooper Huffman and A. W. Ingersoll, *J. Am. Chem. Soc.*, 1951, **73**, 3366.

¶ Hydrogenation performed with Adam's catalyst by the methods of Chilton or Landor.[6]