

Novel Synthesis of Substituted Allenes *via* Organoboration of Alkynylstannanes

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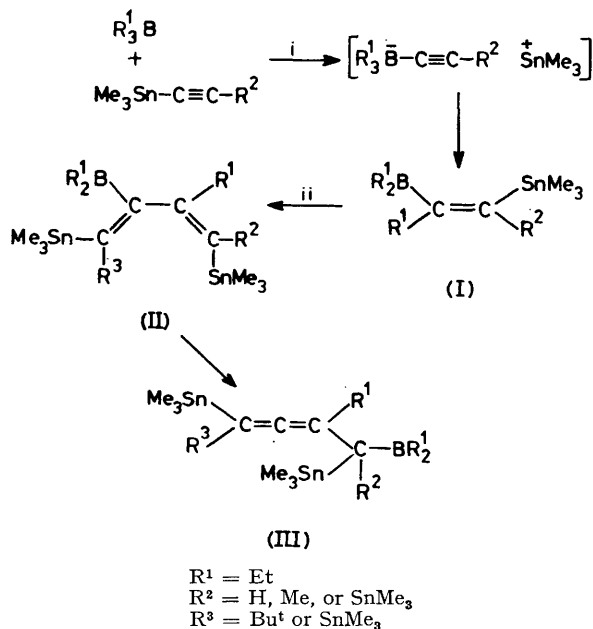
Summary The formation of various substituted allenes in high yields by the reaction of triethylborane with alkynyltrimethylstannanes is reported.

THE preparation and chemistry of allenes is well documented.¹ However, there are not many examples of organo-metallic substituted allenes. We found that some alkynyl-trimethylstannanes, $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{R}$, react with triethylborane to give substituted allenes in high yields (Scheme).

On the basis of n.m.r. spectroscopic data it was concluded that the structure of compound (I) is that given in the Scheme² rather than a *cis*-addition product originally suggested.³ We think that the rearrangements shown in the Scheme are involved in the formation of (I), and in other cases we have found some evidence for the intermediacy of the alkynyltrialkylborate anion.⁴ In any case, the products of the reaction leading to (I) closely resemble those obtained by the reaction between alkynyltrialkylborates and chlorotributylstannane.⁵

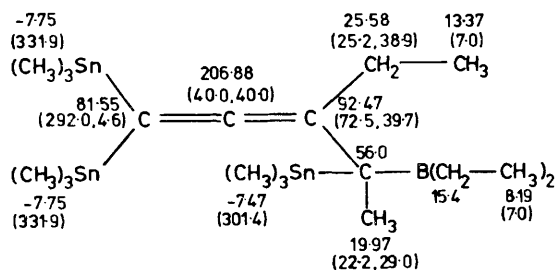
It has been reported⁶ that 2 mol of 1,1-bis(trimethylstannyl)-2-diethylborylbut-1-ene (I; $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{SnMe}_3$) decompose *via* deorganoboration. This leads to an allene (III; $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{R}^3 = \text{SnMe}_3$) and triethylborane. The intermediacy of (II) has been suggested to explain this unexpected result. This assumption is now more firmly supported by the observation that allenes (III; $\text{R}^2 \neq \text{R}^3$) can be prepared in a stepwise synthesis. The compounds (III) are either yellowish oils which can be distilled at 10^{-1} Torr, or colourless crystals (III; $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{R}^3 = \text{SnMe}_3$) which can be recrystallized from pentane at -78°C . They are very soluble in all organic solvents and extremely sensitive towards oxygen.

A reaction pathway similar to the one leading to (I)² may be responsible for the formation of (II) which then rearranges irreversibly to (III) by migration of the diethylboryl group. However, the influence of R^2 and R^3 on the course of the reaction is not clearly understood at present. An essentially quantitative yield of (III) is obtained when $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{H}$ or Me , $\text{R}^3 = \text{Bu}^t$ or SnMe_3 , and $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{R}^3 = \text{SnMe}_3$, while in the case of $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{R}^3 = \text{H}$ or Me mainly products with isolated double bonds are formed which have not yet been unambiguously identified. Similarly, mixtures of these products and (III) are found when $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Me}$ and $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{H}$.



SCHEME. i, Tetrahydrofuran or hexane, 0°C ; ii, $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{R}^3$, $80-120^\circ\text{C}$.

The formation of (III) can be easily monitored by i.r. spectroscopy. A strong sharp band is found in the region 1890–1925 cm^{-1} , characteristic of the $\text{C}=\text{C}=\text{C}$ unit in allenes.⁷ Further evidence for the allene structure stems from ^{13}C n.m.r. spectroscopy showing the typical resonance signal of the allene carbon $=\text{C}=\text{C}=\text{C}$ at very low field (200–210 p.p.m. relative to Me_4Si).⁸ In addition, the coupling constants nJ (^{119}Sn – ^{13}C) serve as a proof for the correct structural assignment. The Figure shows the ^{13}C n.m.r. data



FIGURE

(Received, 10th February 1978; Com. 140.)

¹ (a) H. Fisher in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, London, New York, and Sidney, 1964, p. 1025; (b) D. R. Taylor, *Chem. Rev.*, 1967, **67**, 317; M. Murray in 'Methoden der Organischen Chemie,' Houben-Weyl, Georg Thieme Verlag, Stuttgart, 1977, p. 963.

² G. Menz and B. Wrackmeyer, *Z. Naturforsch.*, 1977, **32b**, 1400.

³ B. Wrackmeyer and H. Nöth, *J. Organometallic Chem.*, 1976, **108**, C21.

⁴ L. Killian and B. Wrackmeyer, *J. Organometallic Chem.*, 1978, **148**, 137.

⁵ J. Hooz and R. Mortimer, *Tetrahedron Letters*, 1976, 805.

⁶ B. Wrackmeyer, *Z. Naturforsch.*, in the press.

⁷ Ref. 1a, p. 1125.

⁸ J. K. Crandell and S. A. Sujka, *J. Amer. Chem. Soc.*, 1972, **94**, 5084; C. Charrier, D. E. Dorman, and J. D. Roberts, *J. Org. Chem.*, 1973, **38**, 2644.

(CDCl_3) for (III; $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{SnMe}_3$); the δ values are in p.p.m. (± 0.05) relative to Me_4Si and the nJ (^{119}Sn – ^{13}C) values are in Hz (± 1) (in parentheses). The coupling constant between carbon and the two tin nuclei attached to the allenic carbon is given in the first place as deduced from the relative intensities of the $^{117/119}\text{Sn}$ satellite signals in the ^{13}C n.m.r. spectrum. The carbon nuclei bound to the boron atom are easily recognized by their broad ^{13}C n.m.r. signals (56.0 and 15.4 p.p.m.) due to the partially relaxed spin–spin coupling between ^{13}C and ^{11}B ($I = 3/2$) and ^{10}B ($I = 3$).

^1H and ^{11}B n.m.r. spectra as well as elemental analyses are in complete agreement with the proposed allene structure.

This new class of allenes promises successful preparation of other allenes by taking advantage of the reactive carbon–tin and carbon–boron bonds in (III).

We are grateful to JEOL for measuring the ^{13}C n.m.r. spectra. Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.