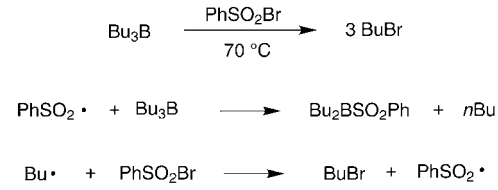
Hydroallylation of Alkenes

Tin-Free Radical Allylation of *B*-Alkylcatecholboranes**

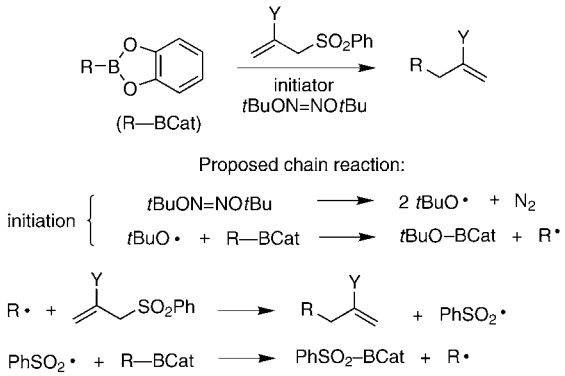
*Arnaud-Pierre Schaffner and Philippe Renaud**

For many years organoboron chemistry has been a privileged field of research for synthetic organic chemists. Following the spectacular development of radical chemistry in organic synthesis,[1] the use of organoboranes has recently led to many novel and useful synthetic applications such as hydroxylation reactions and conjugate additions.[2] These recent reports have shown that *B*-alkylcatecholboranes readily undergo radical substitution at boron and are therefore particularly good precursors for radical chain reactions.[3] However, at the moment, the method is limited mainly to conjugate addition to enones[3a] and to other activated olefins in the presence of a chain-transfer reagent.[3b,e] This last reaction is very general; however, the direct reaction of the radical with the chain-transfer reagent may be an important side reaction with weakly activated alkenes. This problem is well known in radical conjugate addition mediated by tin hydride (Giese reaction),[4] and the reduced radical precursor is a significant side product. In tin chemistry the problem has been solved by the development of the fragmentation method based on the use of allylstannanes.[5] Allylstannanes are employed as a radical trap and as chain-transfer reagents. In this communication we report an efficient fragmentation process for the allylation of organoboranes. *B*-Alkylcatecholboranes, prepared in situ by hydroboration of olefins with catecholborane, can be allylated efficiently with allyl sulfones. This tin-free radical method parallels the allylstannane-mediated radical allylation. Interestingly, this radical approach complements nicely Knochel's procedure for the allylation of organoboranes, which requires transmetalation to organozinc derivatives.[6]

In 1972 Davies and Roberts established that benzenesulfonyl bromide is a suitable reagent for the bromination of tri-*n*-butylborane (Scheme 1).[7] They assumed that this reaction was a radical chain process in which a benzenesulfonyl radical displaces an alkyl radical from tri-*n*-butylborane. Their observation incited us to try a similar radical chain process for the allylation of *B*-alkylcatecholboranes using easily available allyl sulfones (Scheme 2).[8] Since phenyl sulfones are employed, the fragmentation produces a stable phenyl-



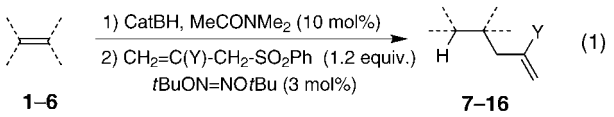
Scheme 1. Bromination of tri-*n*-butylborane according to Davies and Roberts.



Scheme 2. Proposed approach for the radical allylation of *B*-alkylcatecholboranes.

sulfonyl radical that should react with *B*-alkylcatecholborane to sustain the chain reaction. Oxygen-centered radicals react efficiently with *B*-alkylcatecholboranes. Therefore, di-*tert*-butylhyponitrite was chosen as an initiator due to its easy availability and practicability to furnish *tert*-butoxyl radical in refluxing dichloromethane.[9] The thermal properties of this initiator should allow us to run a one-pot hydroboration/radical reaction sequence by taking advantage of the very mild, efficient, and cost-effective hydroboration conditions developed by Fu and Garett.[10]

The whole transformation represents formally a reductive allylation or hydroallylation of alkenes [Eq. (1)]. The reaction was first tested with 2-(methoxycarbonyl)prop-2-en-1-yl



(1)

phenyl sulfone as the radical trap (Y = COOEt). The results are summarized in Table 1. The desired products **7**–**11** were obtained in satisfactory to excellent yields by using only 1.2 equivalents of the allyl sulfones with primary (entries 1, 2), secondary (entries 3, 4), and tertiary alkyl radicals (entry 5). The nonsubstituted allyl sulfones react also under these conditions and provide the volatile allylated products **12** and **13** in moderate yields (entries 6, 7). Finally, other allylic sulfones bearing a sulfonyl group (Y = $PhSO_2$) and a bromine atom (Y = Br) were found to react equally well (entries 8–10). The stereochemical outcome of all these reactions is rationalized in a straightforward manner: the hydroboration

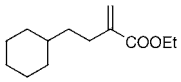
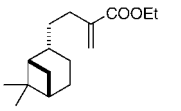
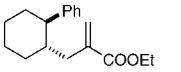
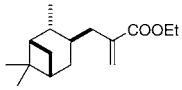
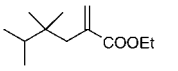
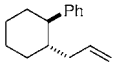
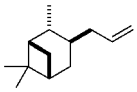
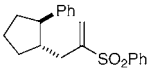
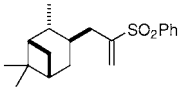
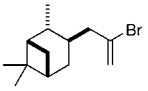
[*] Prof. Dr. P. Renaud, A.-P. Schaffner
University of Berne
Department of Chemisty and Biochemistry
Freiestrasse 3, 3000 Berne 9 (Switzerland)
Fax: (+41) 31-631-3426
E-mail: philippe.renaud@ioc.unibe.ch

[**] This work was supported by the Swiss National Science Foundation (grants 21-67106.01 and 7SUPJ062348). We thank Callery Chemical Company (Pittsburgh) and Z&S Handel AG (Kloten) for the gift of catecholborane.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

  DOI: 10.1002/ange.200351171

Table 1: Reductive allylation of alkenes according to Equation (1).

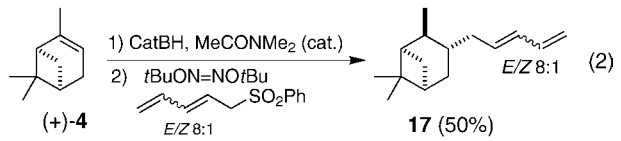
Entry	Alkene		Product		Yield [%]	d.r.
1		**1**		**7**	55	–
2		**2**		**8**	62	90/10
3		**3**		**9**	76	90/10
4		(−)-**4**		**10**	89	96/4
5		**5**		**11**	65	–
6		**3**		**12**	56	90/10
7		(−)-**4**		**13**	52	95/5
8		**6**		**14**	74	97/3
9		(−)-**4**		**15**	89	96/4
10		(−)-**4**		**16**	58	96/4

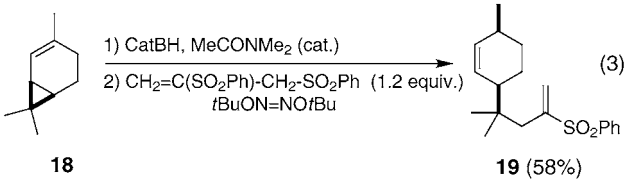
(entries 2, 4, 7, 9, 10) and the radical reaction (entries 3, 4, 6–10) both occur from the less hindered face.

Interestingly, this allylation process seems to be very general. For instance, introduction of a dienyl moiety using penta-2,4-dienyl phenyl sulfone has been achieved [Eq. (2)].[11] The modest yield for the conversion of **4** to **17** (50%) is due to the instability of the dienyl sulfone, which readily polymerizes.[12]

Finally, the radical nature of the process was demonstrated by running an allylation reaction with (+)-2-carene (**18**) [Eq. (3)]. In this radical probe experiment the intermediate cyclopropylmethyl radical undergoes ring opening to give the homoallylic radical, which is trapped by the allylic sulfone to produce **19**. We previously established that in this system no ring opening occurs during the hydroboration step.[13]

In conclusion we have developed a one-pot procedure for the hydroallylation of alkenes. We have demonstrated that *B*-alkylcatecholboranes, easily generated by hydroboration of alkenes with catecholborane, can be allylated with a variety of allyl sulfones by using a fragmentation process. Interestingly, due to the exceptional reactivity of *B*-alkylcatecholboranes towards sulfonyl radicals, excellent yields are obtained with only 1.2 equivalents of the radical trap. The radical nature of the key step is of high interest for further applications of this chemistry in radical cascade reactions for the formation of one or more cycles. Radical chain reactions involving sulfonyl radicals and *B*-alkylcatecholborane are expected to become an important method for tin-free radical reactions.





Experimental Section

General procedure: Catecholborane (0.8 mL, 7.5 mmol) was added dropwise at 0 °C to a solution of olefin (3.0 mmol) and *N*,*N*-dimethylacetamide (28.0 μL, 0.3 mmol) in CH_2Cl_2 (2.0 mL) under nitrogen. The reaction mixture was heated at reflux for 5 h. MeOH (0.20 mL, 4.8 mmol) was added at 0 °C and the solution was stirred for 15 min at room temperature. The sulfone (3.6 mmol) was then added, the solution was warmed at reflux, and di-*tert*-butylhyponitrite (15 mg, 0.09 mmol) was added every hour. The reaction was monitored by GCMS. At the end of the reaction the solution turned to black. The crude product was purified by flash chromatography over silica gel.

Phenyl 1-{[(1*S*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]-methyl}vinyl sulfone (**15**): The reaction was conducted following the general procedure starting from (−)-α-pinene (**4**) (0.409 g, 3 mmol). Flash chromatography (hexane/EtOAc 4:1) afforded **15** (0.848 g, 89%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.93$–7.83 (m, 2H), 7.64–7.45 (m, 3H), 6.41 (s, 1H), 5.80 (s, 1H), 2.52 (dd, $J =$ 15.1, 3.7 Hz, 1H), 2.24 (m, 1H), 2.06 (m, 1H), 1.95–1.69 (m, 3H), 1.54 (m, 1H), 1.23 (m, 2H), 1.13 (s, 3H), 0.93 (m, 3H), 0.86 (s, 3H), 0.61 ppm (d, $J = 9.6$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.3$, 139.2, 133.4, 129.1, 128.2, 124.6, 47.9, 43.7, 41.6, 38.6, 34.1, 34.2, 33.9, 27.9, 22.8, 21.2 ppm. MS (EI): *m*/*z* 319 [M^++1], 246, 218, 177, 137, 81, 55, 41. HRMS (ESI-MS) calculated for $C_{19}H_{27}O_2S$ ([M+1]$^+$): 319.1731; found: 319.1729.

Supporting information for this article (experimental procedures and characterizations of compounds **7**–**17** and **19**) is available on the WWW under http://www.angewandte.org or from the author.

Received: February 13, 2003 [Z51171]

Keywords: allylation · allylic compounds · boron · hydroboration · radical reactions · sulfones

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