B-Alkylcatecholborane-Mediated Radical Reactions

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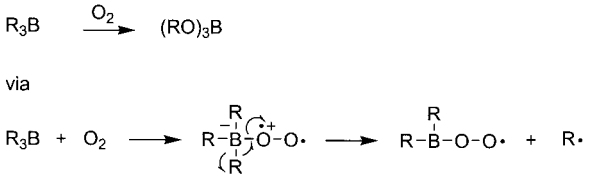
B-Alkylcatecholboranes, easily prepared by hydroboration of alkenes, represent a very efficient source of primary, secondary and tertiary alkyl radicals. The very high sensitivity towards oxygen-and heteroatom-centered radicals makes them particularly attractive for the development of radical chain processes. Very mild conditions for radical hydroxylation of organoboranes using either TEMPO (= 2,2,6,6-tetramethylpiperidine-*N*-oxyl) or oxygen have been developed. Conjugate addition of β-alkylcatecholboranes to enones and enals proceeds very efficiently under oxygen initiation. Inter- and intramolecular addition to other radical traps such as α,β-unsaturated esters, amides and sulfones requires the use of PTOC-OMe {1-[(methoxycarbonyl)oxy]pyridine-2(1*H*)-thione} as a chain transfer reagent. Finally, a very general method for the radical hydroallylation of olefins using allyl sulfones as radical traps is presented. This reaction takes advantage of the very efficient reaction of *B*-alkylcatecholboranes with the benzenesulfonyl radical. The diversity of the chemistry presented in this microreview demontrates that catecholborane represents a very good alternative to tin derivatives for radical reactions involving alkyl radicals.

Introduction

Radical Reactions of Organoboranes

The ability of organoboranes to participate in free radical reactions has been identified since the earliest investigation into their chemistry.[1−3] For instance, the autoxidation of organoboranes (Scheme 1) has been proven to involve radical intermediates.[4,5] This reaction has led recently to the use of triethylborane as a universal radical initiator functioning under a very wide range of reaction conditions (temperature and solvent).[6,7]



Scheme 1. Autoxidation of organoboranes[4,5]

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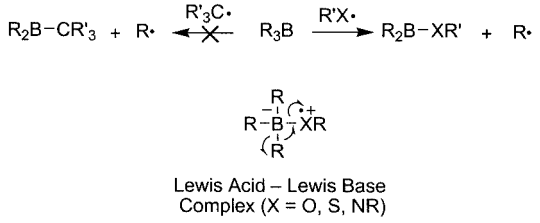
Arnaud-Pierre Schaffner was born in 1976 in Algrange, France. He studied chemistry at the University Louis Pasteur of Strasbourg and received his D.E.A. (Diplôme d'études approfondies) in 2000 in molecular and supramolecular organic chemistry under the direction of Dr. G. Guichard. In 2000, he joined the group of Prof. P. Renaud in Berne, Switzerland, where he obtained his Ph.D. in 2004. His research activity concerned the development of sulfonyl-mediated radical reactions of organoboranes.

Philippe Renaud was born in Neuchâtel in 1959. After his undergraduate study at the University of Neuchâtel, he continued his education at the ETH Zürich, where he received his Ph.D. under the supervision of Prof. D. Seebach in 1986. From October 1986 to December 1987 he was a postdoctoral associate of Prof. M. A. Fox at the University of Texas at Austin. In 1988, he started an independent research program at the University of Lausanne. In 1992, he obtained the Alfred Werner Fellowship which allowed him to continue his research work in Lausanne. In October 1993, he moved to the University of Fribourg as an associate professor. Since March 2001, he is professor of organic chemistry at the University of Bern. His research interests include the development of novel synthetic methods based on radical reactions, the use of Lewis acids for asymmetric reactions and the synthesis of biologically active compounds.

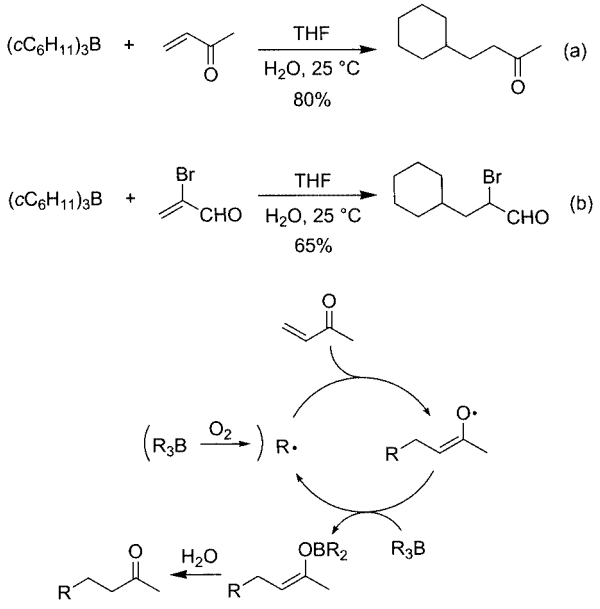
MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

Interestingly, homolytic substitution at the boron atom does not proceed with carbon-centered radicals.[8] However, many different types of heteroatom-centered radicals, for example alkoxyl radicals, react efficiently with the organoboranes (Scheme 2). This difference in reactivity is caused by the Lewis base character of the heteroatom-centered radicals. Indeed, the first step of the homolytic substitution is the formation of a Lewis acid−Lewis base complex between the borane and the radical. This complex can then undergo a β-fragmentation leading to the alkyl radical. This process is of particular interest for the development of radical chain reactions. Very few synthetic applications of this reactivity of organoboranes have been reported.



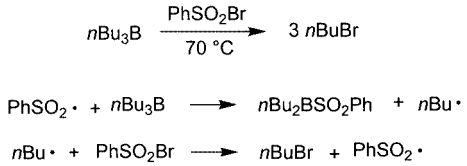
Scheme 2. Reactivity of carbon- and heteroatom-centered radicals towards organoboranes

One of the most important applications of this chemistry is the conjugate addition to enones and enals reported by Brown [Scheme 3, Equations (a) and (b)].[9−12] The proposed mechanism involves the reaction of the intermediate enolate radical with the trialkylborane.[13] One serious drawback of this strategy is that only one of the three alkyl groups is efficiently transferred, so the method is restricted to trialkylboranes derived from the hydroboration of easily available and cheap alkenes. The use of *B*-alkylboracyclanes proposed by Brown and Negishi, referred to later as the Brown−Negishi reaction, provided a partial solution to this problem but proved to be unsatisfactory for the generation of primary alkyl radicals as well as for addition to β-substituted enones.[14]



Scheme 3. The Brown conjugate addition[9−12]

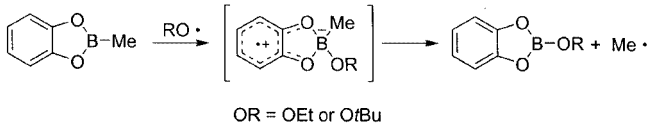
Another interesting reaction was reported in 1972 by Davies and Roberts.[5] They established that benzenesulfonyl bromide is a suitable reagent for the bromination of tri-*n*-butylborane (Scheme 4). They assumed that this reaction was a radical chain process where a benzenesulfonyl radical displaced an alkyl radical from tri-*n*-butylborane.



Scheme 4. Bromination of tri-*n*-butylborane according to Davies and Roberts[5]

B-Alkylcatecholboranes

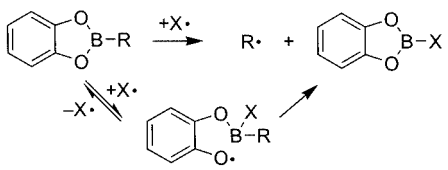
Reactivity of organoboranes towards homolytic substitution by oxygen-centered radical is dependent on the Lewis acidity of the borane. Davies and Roberts have reported the following reactivity order: $R_3B > R_2BOR > RB(OR)_2$ with R = alkyl. Due to π bonding between the boron atom and the oxygen atom, boronic esters are less reactive than trialkylboranes towards alkoxyl radicals. Very interestingly, *B*-alkylcatecholboranes (2-alkylbenzo[*d*][1,3,2]dioxaboroles) behave differently. They are extremely sensitive towards oxygen and they react readily with alkoxyl radicals. It was clearly demonstrated by ESR that the perboryl radical intermediate resulting from the complexation of *B*-methylcatecholborane with the alkoxyl radical is stabilized by delocalization onto the aromatic ring (Scheme 5).[15]



Scheme 5. Reaction of *B*-methylcatecholborane with alkoxyl radicals[15]

The observation of Davies and Roberts regarding the stability of the perboryl radical is at the origin of our own investigations about the use of *B*-alkylcatecholboranes as radical precursors. *B*-alkylcatecholboranes are expected to be more reactive than trialkylboranes and they are easily prepared from olefins by hydroboration with catecholborane with or without a catalyst. However, the most attractive feature of *B*-alkylcatecholboranes is the possibility to generate selectively one alkyl radical from an olefin, a possibility that trialkylboranes do not offer since no selective cleavage of the desired alkyl group is observed (vide supra). Indeed, reaction of *B*-alkylcatecholborane with a heteroatom-centered radical leads in an irreversible manner to the alkyl radical since cleavage of the "wrong" boron−oxygen bond

is a reversible process that finally leads to the irreversible formation of an alkyl radical (Scheme 6).

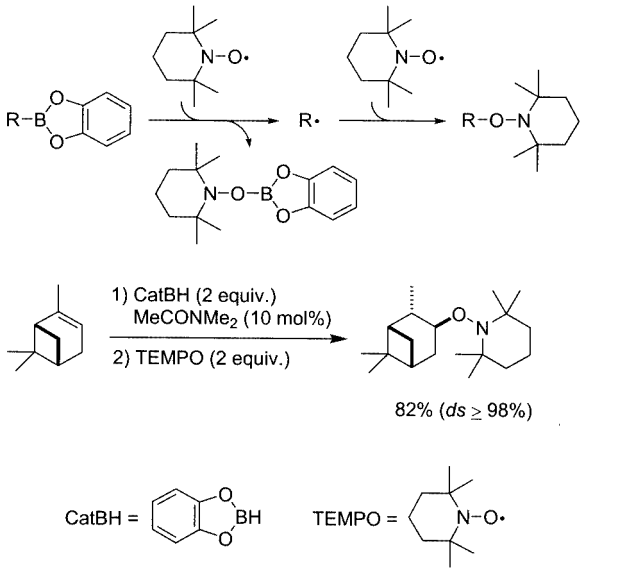


Scheme 6. Irreversible formation of alkyl radicals from *B*-alkylcatecholboranes

Radical Oxygenation using TEMPO

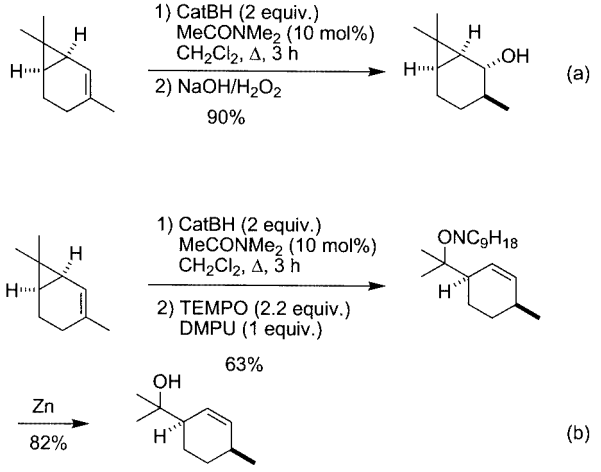
The conversion of alkenes into alcohols by hydroboration followed by oxidative workup by a polar mechanism is characterized by a predictable and high degree of stereoselectivity, high chemical yields and mild and simple experimental conditions which are compatible with a large variety of chemical functions. It is worth noting that very few attempts have been made to develop radical hydroxylation reactions, as they are considered to be less selective and low-yielding methods. In this context, we recently reported a valuable very mild alternative to the classical oxidative treatment to convert olefins into alcohols via the corresponding *B*-alkylcatecholboranes.[16,17] In this procedure, the *B*-alkylcatecholboranes, prepared by hydroboration of the corresponding alkenes with *N*,*N*-dimethylacetamide as catalyst,[18] were treated with 2 equiv. of TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl), a stable persistent radical (Scheme 7).[19] The reaction affords in good to excellent yield the corresponding alkoxyamine. The first equivalent of TEMPO is used to generate the alkyl radical from the organoborane, the second equivalent is acting as a radical trap to form an alkoxyamine that can be reduced using standard methods to the desired alcohol. The stereochemical outcome of the reaction corresponds very well to expectations for radical reactions. For instance, the hydroboration of α-pinene affords the alkoxyamine with an excellent diastereoselectivity (Scheme 7). In this process, the first new chiral center is controlled during the hydroboration step and the second one during the reaction of the secondary alkyl radical with TEMPO. This is an interesting case of stereoselective coupling of two radicals; the bulkiness of TEMPO is at the origin of this stereocontrol. This reaction illustrates very well the increased reactivity of the *B*-alkylcatecholborane derivatives relative to trialkylboranes. Indeed, attempts to oxidize trialkylboranes by TEMPO failed unless a stoichiometric amount of di-*tert*-butyl hyponitrite was used as an initiator.[20]

With specific substrates, the radical-mediated oxidation of organoboranes is leading to products that differ from those obtained under classical oxidation. For example, the hydroboration of 2-carene with catecholborane followed by treatment with H_2O_2/NaOH afforded a bicyclic alcohol according to Scheme 8 [Equation (a)].[21] Interestingly, the TEMPO oxidation of the same intermediate followed by



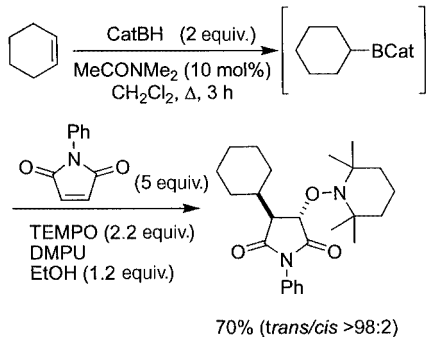
Scheme 7. Oxygenation of *B*-alkylcatecholborane using TEMPO[16,17]

zinc-mediated reduction of the alkoxylamine give the monocyclic tertiary alcohol resulting from the ring-opening of the intermediate cyclopropylalkyl radical [Scheme 8, Equation (b)].[16,17]



Scheme 8. Classical (H_2O_2, NaOH) versus radical oxidation of *B*-alkylcatecholboranes[16,17]

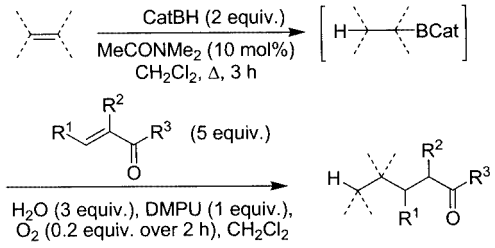
Alkyl radicals generated from *B*-alkylcatecholboranes and TEMPO have also been used for conjugate addition. This tandem process requires again the use of 2 equiv. of TEMPO, the first one to generate an alkyl radical that adds to the activated olefin and the second one to trap the radical adduct. A typical example of this reaction is shown in Scheme 9; again the reaction is highly *trans*-selective (*trans*/*cis* = 98:2). However, this reaction is limited to radical addition to highly reactive olefins because TEMPO reacts rapidly with the initial radical.



Scheme 9. The use of *B*-alkylcatecholboranes and TEMPO in conjugate addition[17]

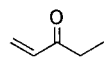
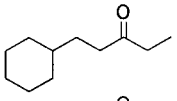
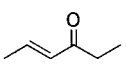
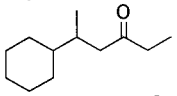
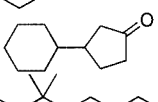
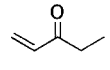
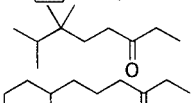
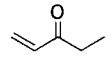
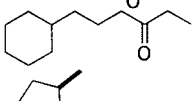
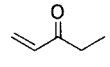
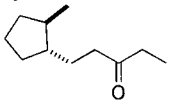
Conjugate Addition to Enones and Enals

The Brown−Negishi reaction is not suitable for primary alkyl radicals (yield < 35%) and for radical traps substitued at the β-position (vide supra).[14] An approach based on catecholborane was expected to solve these two problems. Indeed, we have demonstrated that *B*-alkylcatecholboranes can be used as radical precursors in the presence of oxygen for conjugate addition to a wide range of α,β-unsaturated aldehydes and ketones according to Scheme 10.[22] Some



Scheme 10. Conjugate addition of *B*-alkylcatecholborane to enones[22]

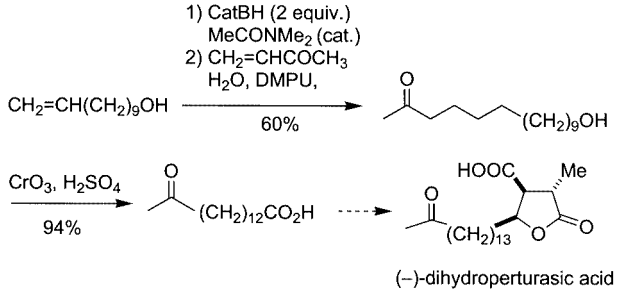
Table 1. Conjugate addition of *B*-alkylcatecholborane to enones according to Scheme 10[22]

Entry	Alkene	Radical trap	Product	Yield
1				94%
2				74%
3				86%
4				71%
5				69%
6				88%[a]

[a] *trans*/*cis* = 91:9.

typical results are presented in Table 1. Radical addition to ethyl vinyl ketone gives the product of conjugate addition in excellent yield (Table 1, Entry 1). β-Substituted enones such as methyl prop-1-en-1-yl ketone and cyclopentanone also works very well (Entries 2 and 3). Radical addition of tertiary alkyl radical is also efficient (Entry 4). The reaction also proved to be efficient with primary alkyl radicals generated from a terminal alkene (Entry 5). Finally, the stereochemical outcome of these reactions fits well with the data reported for related radical reactions (Entry 6).[23,24]

The conjugate addition of *B*-alkylcatecholboranes generated in situ from alkenes to enals and enones compares favorably with classical procedures involving organocuprate chemistry. For instance, we have prepared on a 50-mmol scale 14-oxopentadecanoic acid, a key intermediate in the synthesis of (−)-dihydropertusaric acid, from unprotected undec-10-en-1-ol by hydroboration/conjugate addition followed by Jones oxidation (Scheme 11).[25]

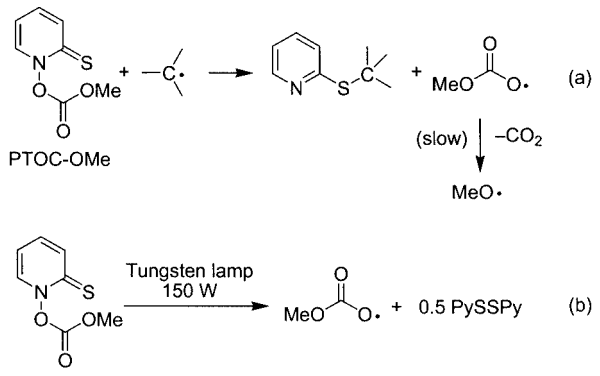


Scheme 11. Preparation of 14-oxopentadecanoic acid from unprotected undec-10-en-1-ol[25]

Conjugate Addition to Activated Olefins

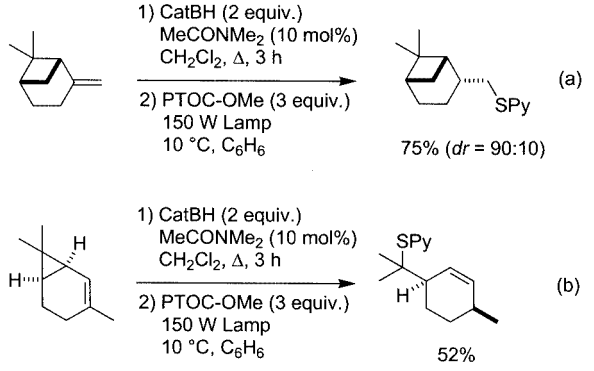
The modified Brown−Negishi conjugate addition described above is limited to enone and enal radical traps. Other radical traps such as unsaturated esters, amides and sulfones fail to react under these conditions. This failure was interpreted as a consequence of an inefficient reaction of the radical adduct and β-alkylcatecholboranes. This inefficiency is caused by the insufficient density of unpaired electrons on the oxygen atom of theses radicals relative to ketone enolate and aldehyde enolate radicals. The use of a chain transfer reagent which is able to convert a carbon-centered radical into an oxygen-centered radical allows to solve this problem. The Barton carbonate PTOC-OMe {1-[(methoxycarbonyl)oxy]pyridine-2(1*H*)-thione}[26,27] proved to be an excellent radical chain transfer reagent according to Scheme 12 [Equation (a)].[28] Interestingly, the same reagent prove to be an excellent initiator under irradiation with a standard 150-W tungsten lamp [Scheme 12, Equation (b)]; PTOC-OMe is a stable reagent easily obtained by the reaction of the commercially available sodium salt of 1-hydroxypyridine-2(1*H*)-thione with methyl chloroformate.[29]

In a preliminary study, in situ generated *B*-alkylcatecholboranes were allowed to react with PTOC-OMe under



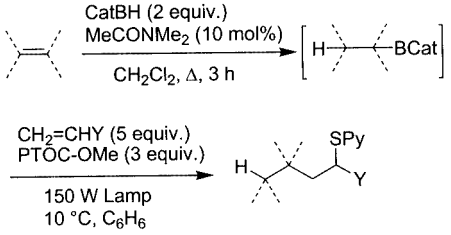
Scheme 12. Barton carbonate, PTOC-OMe, a radical chain transfer reagent able to convert a *C*-centered radical into an *O*-centered radical (a) and a radical initiator (b)[28]

irradiation with a standard 150-W lamp. The *S*-pyridyl products coming from primary, secondary and tertiary alkyl radicals were isolated in moderate to good yields. A typical example starting from β-pinene is shown in Scheme 13 [Equation (a)]. The radical nature of this reaction is proved by the reaction with 2-carene, which gives the product of ring-opening of the cyclopropane in 52% yield [Scheme 13, Equation (b)].



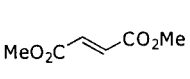
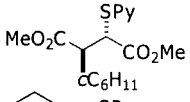
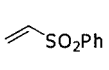
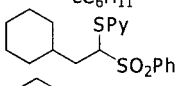
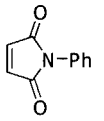
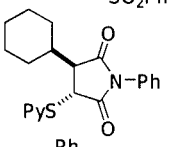
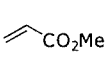
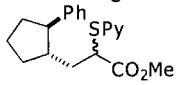
Scheme 13. Radical sulfurization with PTOC-OMe[28]

Based on these initial results, a procedure for conjugate addition to various activated alkenes was developed. A one-pot procedure involving hydroboration of an alkene with catecholborane followed by irradiation in the presence of 5 equiv. of an activated alkene and 3 equiv. of the chain transfer reagent PTOC-OMe was developed (Scheme 14).[28] Representative results are summarized in Table 2.



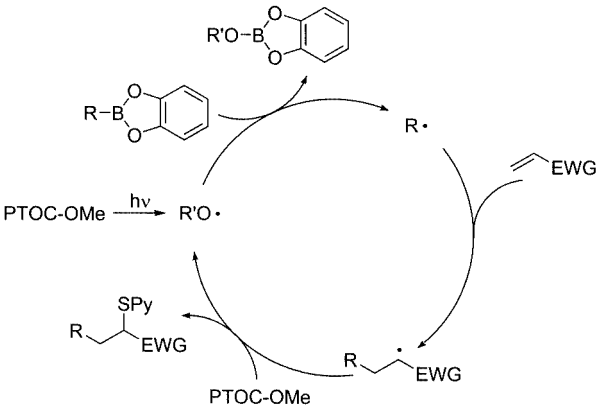
Scheme 14. PTOC-OMe-mediated conjugate addition of *B*-alkylcatecholborane to activated alkenes[28]

Table 2. PTOC-OMe-mediated conjugate addition of *B*-alkylcatecholborane to activated alkenes according to Scheme 14[28]

Entry	Alkene	Radical trap	Product	Yield
1				94%[a]
2				75%
3				81%[b]
4				61%[c]

[a] *anti*/*syn* = 77:23. [b] *trans*/*cis* = 98:2. [c] *trans*/*cis* = 97:3.

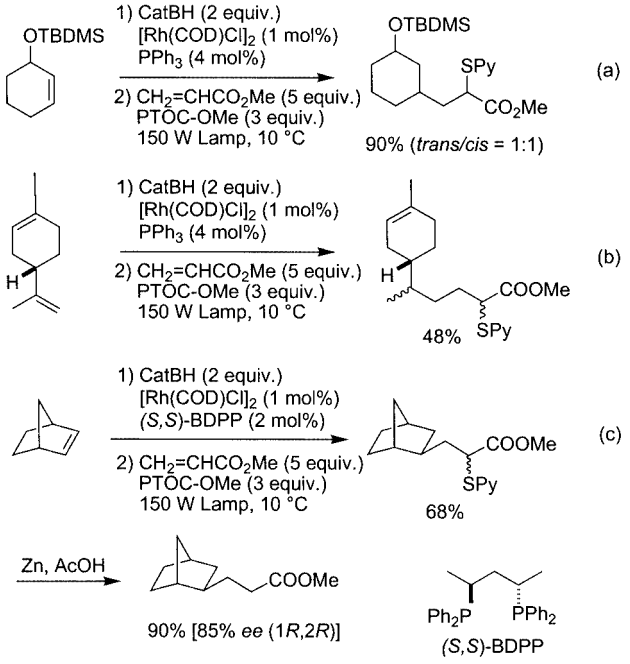
In contrast to the tin hydride mediated reaction (Giese reaction),[30] no slow addition of the chain carrier is necessary. This is easily understandable from the reaction mechanism depicted in Scheme 15. In the Giese reaction, the tin hydride reduces the initial alkyl radical and the radical adduct at approximatively the same rate. Therefore, in order to favor the product of conjugate addition, it is compulsory to work with low concentrations of tin hydride. In the catecholborane-mediated reaction, the initial radical reacts much slower than the radical adduct with the PTOC-OMe chain transfer reagent. Indeed, a nucleophilic alkyl radical adds more slowly to the sulfur atom of a thiocarbonyl group than a radical having a marked electrophilic character such as the radical adduct.



Scheme 15. Radical chain mechanism for the conjugate addition of *B*-alkylcatecholboranes to activated olefins [R = alkyl group; EWG = electron-withdrawing group; R′O· = MeOC(O)O·, MeO·][28]

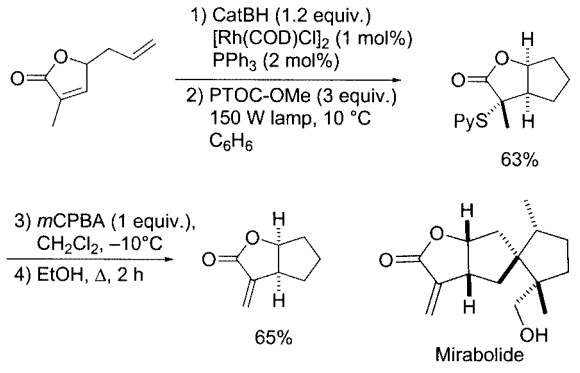
B-Alkylcatecholboranes, prepared by rhodium(I)-catalyzed hydroboration of alkenes, are suitable radical precursors for conjugate addition to activated olefins (Scheme 16). This procedure proved to be particularly useful for the control of the regio- [Equation (a)] and chemoselectivity [Equa-

tion (b)] of such tandem processes.[31] For these two reactions, the use of *N,N*-dimethylacetamide gave unsatisfactory results. One-pot enantioselective hydroboration/radical conjugate addition has also been successfully performed. For example, the reaction between norbornene and methyl methacrylate as radical trap afforded the product of conjugate addition in 68% yield and 85% *ee* (after desulfurization) using $[Rh(COD)Cl]_2$ and the chiral diphosphane (*S,S*)-BDPP as catalyst for the hydroboration step [Scheme 16, Equation (c)].



Scheme 16. Control of the chemo-, regio- and enantioselectivity by rhodium(I)-catalyzed hydroboration[31]

The rhodium-catalyzed hydroboration has opened the way to cyclization reactions starting from dienes.[32] For instance, rhodium-catalyzed hydroboration of the terminal alkenyl group of an α,β-unsaturated lactone followed by reaction with the PTOC-OMe chain transfer reagent afforded the bicyclic α-*S*-pyridyllactone in 63% yield (Scheme 17). After oxidation of the sulfide with *m*CPBA, thermal elimination of the sulfoxide afforded the corresponding α-methylene lactone in 65% yield. Interestingly, such bicyclic α-methylenelactones are substructures that can be found in many natural products such as mirabolide.[33]



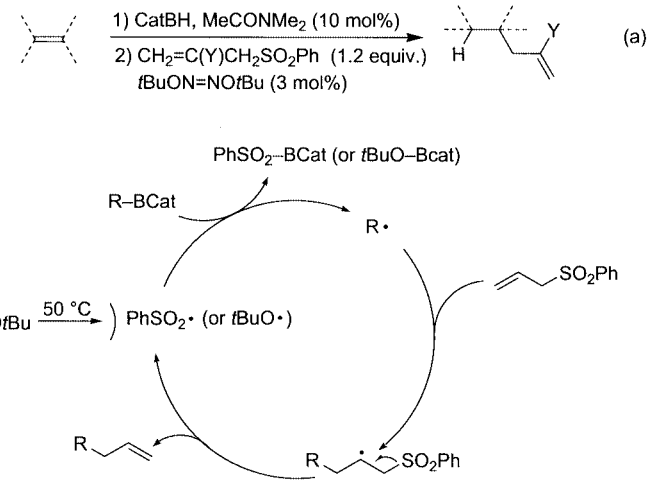
Scheme 17. Preparation of α-methylenelactone related to mirabolide by catecholborane-mediated radical cyclization[32]

Radical Allylation

The bromination of tributylborane with benzenesulfonyl bromide described by Davies and Roberts[5] (Scheme 4) incited us to examine the possibility of running a similar radical chain process for the allylation of *B*-alkylcatecholboranes using easily available allyl sulfones.[34] By using phenyl sulfones, the fragmentation produces a stable phenylsulfonyl radical that should react with *B*-alkylcatecholborane to sustain the chain reaction (Scheme 18). Oxygen-centered radicals react efficiently with *B*-alkylcatecholboranes. Therefore, the easily available di-*tert*-butyl hyponitrite was selected as an initiator due to its ability to furnish the *tert*-butoxyl radical at the reflux temperature of dichloromethane. The thermal properties of this initiator should allow 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.[18] The whole transformation represents formally a reductive allylation or hydroallylation of alkenes [Scheme 18, Equation (a)].

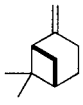
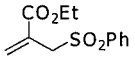
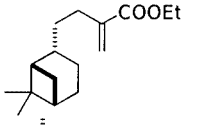
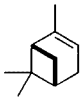
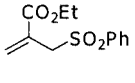
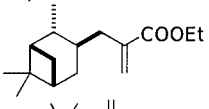
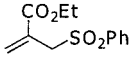
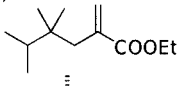
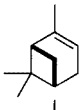
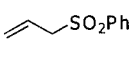
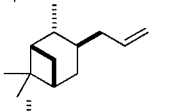
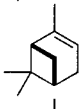
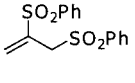
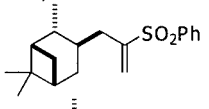
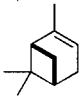
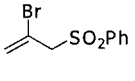
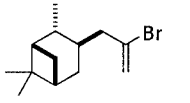
Typical results are shown in Table 3. The desired products were obtained in satisfactory to excellent yields by using only 1.2 equiv. of the allyl sulfones with primary, secondary and tertiary alkyl radicals (Entries 1−3). The nonsubstituted allyl sulfone also reacts under these conditions and provides the volatile allylated product in moderate isolated yield (Entry 4). Finally, other allylic sulfones bearing a sulfonyl group (Y = $PhSO_2$) and a bromine atom (Y = Br) were found to react equally well (Entries 5−6). The stereochemical outcome of all these reactions is rationalized in a straightforward manner, both the hydroboration and the radical reaction are occurring from the less hindered face of the alkene and of the radical, respectively.

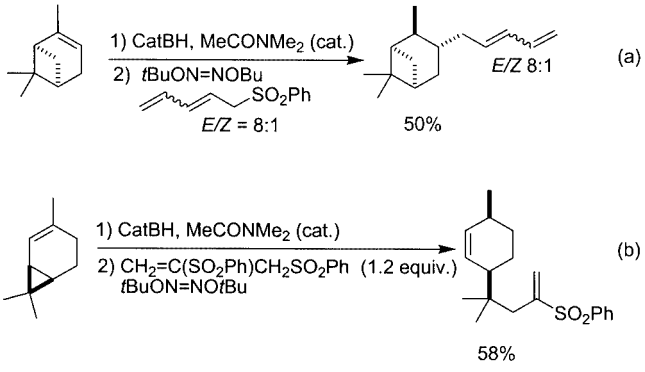
Interestingly, this allylation process seems to be very general. For instance, introduction of a dienyl moiety using penta-2,4-dienyl phenyl sulfone has been achieved [Scheme 19, Equation (a)]. The modest yield (50%) for the conversion is due to the instability of the dienyl sulfone which readily polymerizes. Finally, the radical nature of the process has been demonstrated by running an allylation reaction with (+)-2-carene [Scheme 19, Equation (b)]. In this radical probe experiment, the intermediate cyclopropylmethyl radical undergoes ring opening to a homoallylic radical that is trapped by the allylic sulfone to afford the corresponding monocyclic compound in 58% yield. We have previously established that, in this system, no ring opening is occurring during the hydroboration step [Scheme 8, Equation (a)].



Scheme 18. Radical hydroallylation of alkenes[34]

Table 3. Radical hydroallylation of alkenes according to Scheme 18 [Equation (a)][34]

Entry	Alkene	Allyl sulfone	Product	Yield	*dr*
1				62%	90:10
2				89%	96:4
3				65%	–
4				52%	95:5
5				89%	96:4
6				58%	96:4



Scheme 19. Introduction of a dienyl moiety using penta-2,4-dienyl phenyl sulfone [Equation (a)] and hydroallylation of (+)-2-carene [Equation (b)][34]

Conclusion

B-Alkylcatecholboranes, easily generated by hydroboration with catecholborane, are very efficient precursors of alkyl radicals. They have been applied to many different transformations such as hydroxylation, conjugate addition to enones and enals, conjugate addition to other radical traps followed by sulfurization.[35] Finally, allylation reactions using the β-fragmentation of a benzenesulfonyl radical has been reported. The efficient reaction between the benzenesulfonyl radical and *B*-alkylcatecholboranes opens a whole range of new applications. Aside from the reported allylation, alkenylation, alkynylation as well as halogenation and chalcogenation are currently under investigation and will be reported in a near future. So far, the catecholborane procedure is one of the most general and efficient methods of running tin-free radical reactions. Studies towards the development of polymer-supported reagents as well as extension of this chemistry to different radical reactions are underway.

Acknowledgments

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