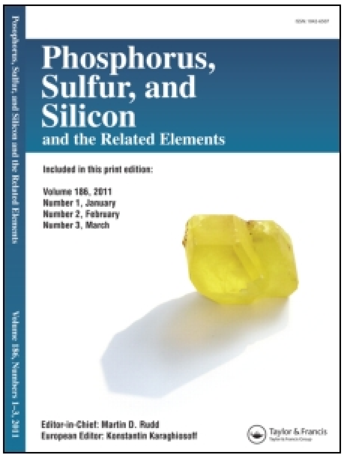

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α,β-Unsaturated α'-Halomethylsulfones: Prepackaged Ramberg–Bäcklund Reagents for Tandem Synthetic Processes

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The synthesis and reactions of several α,β-unsaturated chloromethyl sulfones are presented, for example [(chloromethyl) sulfonyl]-1,3-propadiene, [(chloromethyl) sulfonyl]ethene, [(dichloromethyl)sulfonyl]ethene and (E,Z)-1,2-bis[(chloromethyl)-sulfonyl]ethene. These compounds serve as "prepackaged" Ramberg–Bäcklund reagents, which, following an appropriate first step, such as Diels–Alder addition, react with a base, giving Ramberg–Bäcklund products.

Keywords α-Halosulfones; alkene synthesis; Ramberg–Bäcklund reaction

INTRODUCTION

The Ramberg–Bäcklund (RB) reaction is a synthetically useful process in which α-haloalkyl sulfones afford olefins upon treatment with a base. As shown in Scheme 1, the requisite α-haloalkyl sulfones are typically prepared in multistep processes.[1,2] We sought "prepackaged" RB reagents that incorporate all of the components required for the RB reaction into one reactive unit, requiring only an olefinic substrate and base to give olefinic end products with an increase in total number of carbon atoms. In 1983 we described the use of bromomethanesulfonyl bromide ($BrCH_2SO_2Br$, **1**) as a one-carbon example of such a prepackaged reagent (Scheme 2).[3] Reagent **1** readily undergoes light-induced free radical addition to alkenes. Dehydrobromination of the addition

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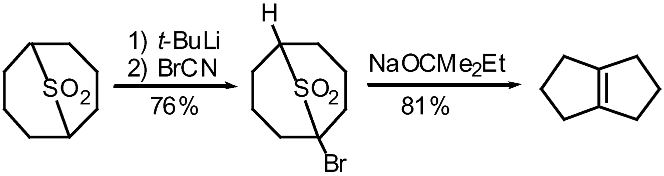
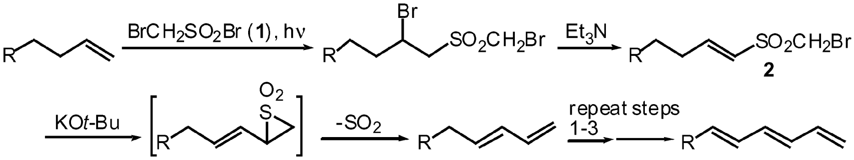


SCHEME 1



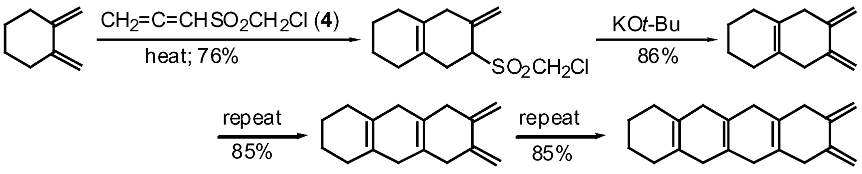
SCHEME 2

products gives α,β-unsaturated α'-bromoalkyl sulfones **2**, which undergo vinylogous RB reaction, giving 1,3-dienes as E,Z-mixtures. Repetition of the process gives isomeric 1,3,5-trienes. Reaction of **1** with 1,3-butadiene followed by dehydrobromination affords 1,3-butadienyl bromomethylsulfone ($CH_2{=}CHCH{=}CH_2SO_2CH_2Br$, **3**). The latter compound can be considered as a five-carbon prepackaged RB reagent because it undergoes Michael-induced RB reactions, for example with sodium isopropoxide, giving *i*-PrO—$CH_2CH{=}CHCH{=}CH_2$.[3]

In a 1972 communication, 1-bromo-1-(methylsulfonyl)ethene ($CH_2{=}C(Br)SO_2CH_3$), which can be considered to be a three-carbon prepackaged RB reagent, was reported to undergo Diels–Alder addition followed by RB reaction, although only a single reaction was described.[4] We sought to further develope α,β-unsaturated α'-halomethylsulfones akin to **2** and **3** as prepackaged RB reagents, focusing in particular on tandem processes, for example where the RB reagent undergoes a pericyclic reaction followed by a RB reaction upon addition of a base.

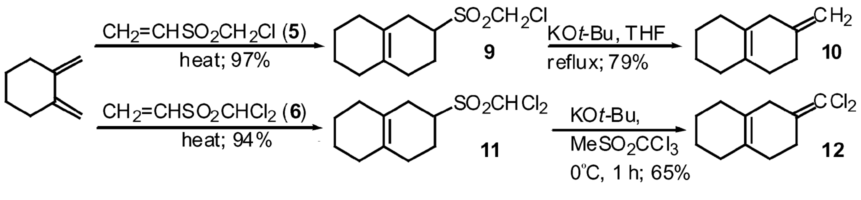
RESULTS

We find that the four-carbon prepackaged RB reagent [(chloromethyl)-sulfonyl]-1,2-propadiene ($CH_2{=}C{=}CHSO_2CH_2Cl$, **4**; Scheme 3), upon tandem Diels–Alder RB reaction, gives the formal Diels–Alder adducts of buta-1,2,3-triene.[5] Reagent **4** has been employed in syntheses of [*n*]beltenes.[6] Use of [(trichloromethyl)sulfonyl]-1,2-propadiene ($CH_2{=}C{=}CHSO_2CCl_3$) as a 1,1-dichloro-1,2,3-butatriene synthon has also been described.[7]



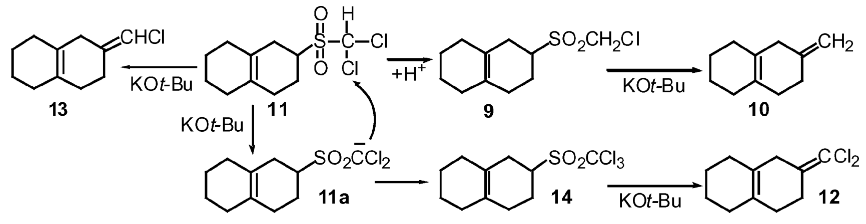
SCHEME 3

We recently described the syntheses and applications of the three- and four-carbon pre-packaged RB reagents [(chloromethyl)-sulfonyl]ethene ($CH_2{=}CHSO_2CH_2Cl$, **5**), [(dichloromethyl)sulfonyl]-ethene ($CH_2{=}CHSO_2CHCl_2$, **6**), (*E*,*Z*)-1,2-bis[(chloromethyl)sulfonyl]-ethene ($ClCH_2SO_2CH{=}CHSO_2CH_2Cl$, **7**), and [(chloromethyl)sulfonyl]ethyne (**8**).[5,8] To prepare **5**, chloromethanesulfenyl chloride ($ClCH_2SCl$) was added to ethylene, giving the known[9] 1-chloro-2-[(chloromethyl)thio]ethane (90%), which was oxidized with two equivalents of *m*CPBA to 1-chloro-2-[(chloromethyl)sulfonyl]ethane. The latter is directly stirred with aqueous $NaHCO_3$, giving **5** (99%) as a colorless oil. A similar sequence of steps was used to convert Cl_2CHSCl (from chlorination of $ClCH_2SCl$)[10] into **6** (78%) by way of 1-chloro-2-[(dichloromethyl)-thio]ethane and 1-chloro-2-[(dichloromethyl)sulfonyl]ethane, neither of which is isolated. Both **5** and **6** readily add to a variety of 1,3-dienes, giving high yields of the corresponding Diels–Alder adducts, for example **9** and **11** as shown in Scheme 4. As anticipated, treatment of the Diels–Alder adducts of **5** with KO*t*-Bu/THF give good yields of the diene-allene adducts, for example **10**, *via* Ramberg–Bäcklund reaction.



SCHEME 4

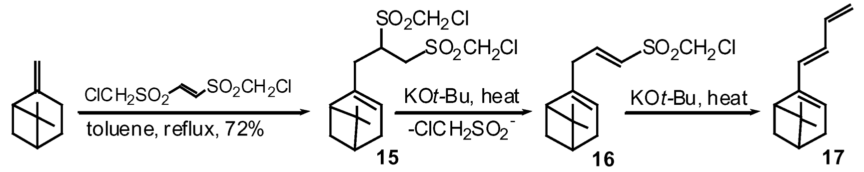
Base treatment of adducts of **6** gave mixtures of the isomeric adducts of chloropropa-1,2-diene together with lesser amounts of the adducts of allene and 1,1-dichloropropa-1,2-diene (**13**, **10**, **12**, respectively, Scheme 5). The latter two compounds are presumably formed by nucleophilic attack of the *α*-sulfonyl-*α*-chlorocarbanion **11a** of the Diels–Alder adduct **11** of **6** on the chlorine of a second adduct molecule, giving [(trichloromethyl)sulfonyl]ethene adduct **14**, which is not isolated.



SCHEME 5

We reasoned that if base treatment of Diels–Alder adducts of **6** were conducted in the presence of an excess of a suitably reactive source of chlorine, chlorine transfer might be possible *prior* to the Ramberg–Bäcklund reaction, leading to exclusive formation of Diels–Alder adducts of 1,1-dichloropropa-1,2-diene. To test this hypothesis, [(trichloromethyl)sulfonyl]methane, $MeSO_2CCl_3$, was used as a novel chlorine source. This little studied compound[11] was conveniently prepared in 91% yield by bubbling Cl_2 into a refluxing, UV-irradiated solution of dimethyl sulfone in SO_2Cl_2. We were pleased to find that when Diels–Alder adducts of **6** were treated at 0°C with KO*t*-Bu-THF in the presence of two equivalents of $MeSO_2CCl_3$, the corresponding Diels–Alder adducts of 1,1-dichloropropa-1,2-diene were formed in good yield (*e.g.*, **12**, Scheme 5).

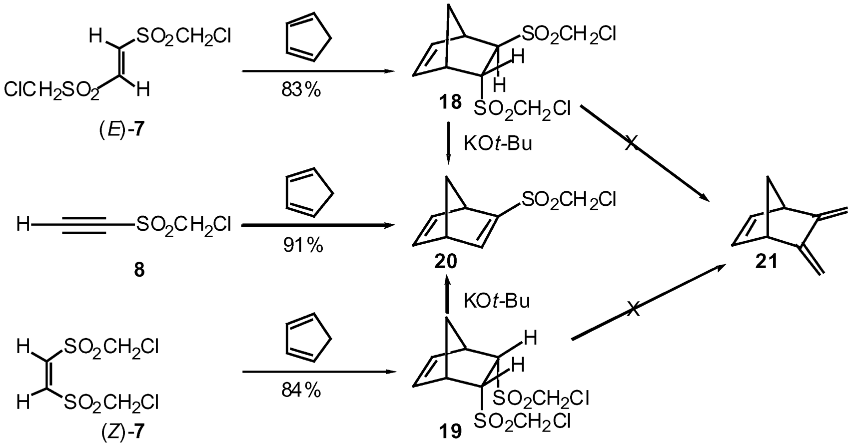
Because compound **7** showed good reactivity as a dienophile (see the following), we examined its reactivity in the ene reaction. When (*E*)-**7** was heated with two equivalents of *β*-pinene in toluene at 135°C for 1.5 h, the ene product 2-{[(1′,2′-bis(chloromethyl)sulfonyl]propyl}-6,6-dimethylbicyclo[3.1.1]hept-2-ene (**15**) was formed in 72% yield as a crystalline solid. Base treatment (*t*–BuOK) of **15** in refluxing THF afforded (*E*)-2-(buta-1,3-dienyl)-6,6-dimethylbicyclo[3.3.1] hept-2-ene (**17**) in low yield. If treatment with base was conducted at 0°C, low yields of 2-[(3-chloromethyl)sulfonyl]allyl-6,6-dimethylbicyclo[3.3.1]hept-2-ene (**16**) could be isolated, leading to the overall proposed mechanism shown in Scheme 6. Although not of



SCHEME 6

synthetic utility because of the low yield, the reaction in Scheme 6 represents the first example of a tandem reaction sequence incorporating an ene reaction with a Ramberg–Bäcklund reaction.

Both (*E*)- and (*Z*)-**7** readily form Diels–Alder adducts (**18** and **19**, respectively) with 1,3-cyclopentadiene (Scheme 7). Base treatment of the adducts gave unstable 2-[(chloromethyl) sulfonyl]bicyclo[2.2.1]hepta-2,5-diene (**20**) rather than 5,6-bis(methylene)bicyclo[2.2.1]hept-2-ene (**21**). Thus, 1,2-elimination from the activated α-sulfonyl carbanions is favored over 1,3-elimination (RB reaction), even with the adduct of (*Z*)-**7**, where a coplanar 1,2-elimination transition state is impossible. Compound **20** could be directly prepared in high yield from Diels–Alder addition of [(chloromethyl)sulfonyl]ethyne (**8**) to cyclopentadiene.



SCHEME 7

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