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Prepackaged Ramberg–Bäcklund reagents: useful tools for organic synthesis

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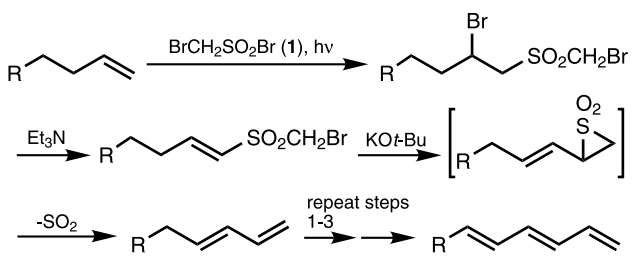
Dedicated to Professor Dieter Seebach on the occasion of the 2003 Tetrahedron Prize with admiration and respect for his many seminal contributions to chemistry, particularly his elegant work in the fields of organosulfur and organoselenium chemistry which has served as an inspiration for our own work

Abstract—The synthesis and reactions of several α,β-unsaturated chloromethyl sulfones is presented, for example [(chloromethyl)-sulfonyl]-1,3-propadiene (**4**), [(chloromethyl)sulfonyl]ethene (**5**), [(dichloromethyl)sulfonyl]ethene (**6**) and (*E*,*Z*)-1,2-bis[(chloromethyl)-sulfonyl]ethene (**7**). These compounds serve as 'prepackaged' Ramberg–Bäcklund reagents, which following an appropriate first step, such as Diels–Alder addition, react with base giving Ramberg–Bäcklund products.

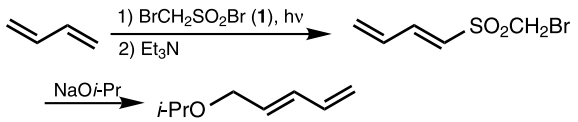
1. Introduction

'Prepackaged' Ramberg–Bäcklund reagents may be defined as compounds having sulfonyl and α-halogen groups which, following an appropriate first step, require only base to give by Ramberg–Bäcklund ('RB') reaction[1] 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 1).[2] Reagent **1** readily undergoes light-induced free radical addition to alkenes. Dehydrobromination of the addition products followed by vinylogous RB reaction gives 1,3-dienes as *E*,*Z*-mixtures. Repetition of the process gives isomeric 1,3,5-trienes.

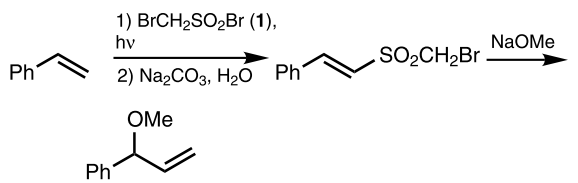
1-[(Bromomethyl)sulfonyl]-1,3-butadiene, from sequential reaction of 1,3-butadiene with **1** and triethylamine, undergoes vinylogous Michael-induced RB ('MIRB') reaction with sodium isopropoxide giving (*E*/*Z*)-1-isopropoxy-2,4-pentadiene (Scheme 2).[2e] A related sequence involving the adduct of **1** with styrene has been reported (Scheme 3).[3] Reagent **1** adds to reactive single bonds giving adducts which undergo the RB reaction (Scheme 4).[4]



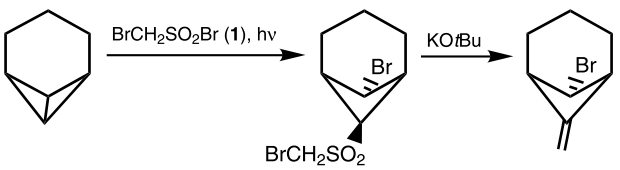
Scheme 1. Use of $BrCH_2SO_2Br$ (**1**) as a prepackaged RB reagent in an iterative process affording 1,3,5-trienes.



Scheme 2. Addition of **1** to 1,3-butadiene with dehydrobromination and Michael-induced Ramberg–Bäcklund (MIRB) reaction with NaO*i*-Pr.



Scheme 3. Addition of **1** to styrene followed by dehydrobromination and MIRB reaction with NaOMe.



Scheme 4. Addition of **1** to a strained single bond and then RB reaction.

Keywords: Ramberg–Bäcklund reaction; α-Halosulfones.
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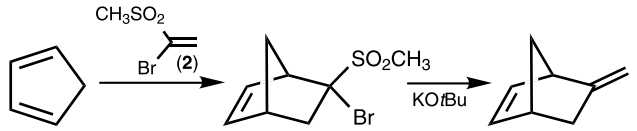
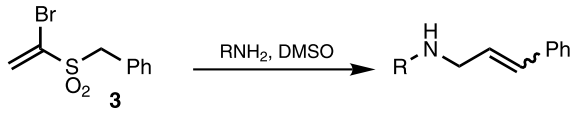


Scheme 5. Tandem Diels–Alder RB reaction of $CH_2{=}C(Br)SO_2CH_3$ (**2**).

An example of a three-carbon prepackaged RB reagent, 1-bromo-1-(methylsulfonyl)ethene ($CH_2{=}C(Br)SO_2CH_3$, **2**) was reported in 1972 (Scheme 5).[5] In this case, reagent **2** underwent Diels–Alder addition followed by RB reaction. A MIRB reaction (Scheme 6) involving benzyl 1-bromovinyl sulfone ($CH_2{=}C(Br)SO_2CH_2Ph$, **3**) with various nucleophiles has recently been described.[6] In a preliminary report in 1990 we showed that the four-carbon prepackaged RB reagent [(chloromethyl)sulfonyl]-1,2-propadiene ($CH_2{=}C{=}CHSO_2CH_2Cl$, **4**) upon tandem Diels–Alder RB reaction gives the formal Diels–Alder adducts of buta-1,2,3-triene.[7] In a more recent preliminary report we describe the syntheses and applications of the three- and four-carbon prepackaged RB reagents [(chloromethyl)-sulfonyl]ethene ($CH_2{=}CHSO_2CH_2Cl$, **5**), [(dichloromethyl)sulfonyl]ethene ($CH_2{=}CHSO_2CHCl_2$, **6**), and (*E*,*Z*)-1,2-bis[(chloromethyl)sulfonyl]ethene ($ClCH_2SO_2$-$CH{=}CHSO_2CH_2Cl$, **7**), respectively.[8] Our full experimental results on these and related studies on prepackaged RB reagents are reported here.



Scheme 6. MIRB reaction of $CH_2{=}C(Br)SO_2CH_2Ph$ (**3**).

2. Results and discussion

2.1. Synthesis of potential prepackaged Ramberg–Bäcklund reagents

Figure 1 gives a sampling of the α,β-unsaturated chloromethyl sulfones we wished to examine as possible prepackaged RB reagents. The examples include the above described allenyl (**4**) and ethenyl (**5**-**7**) chloromethyl sulfones, as well as chloromethyl ethynyl sulfone (**8**) and 1-[(chloromethyl)sulfonyl]-1-haloethenes ($CH_2{=}C(X)SO_2$-CH_2Cl, **9a**,**b**; X=I or F, respectively). While a single example of a dichloromethyl sulfone (**6**) is also included, in the other cases dichloromethyl and trichloromethyl groups could also replace the chloromethyl groups. None of these compounds were known at the inception of this work.

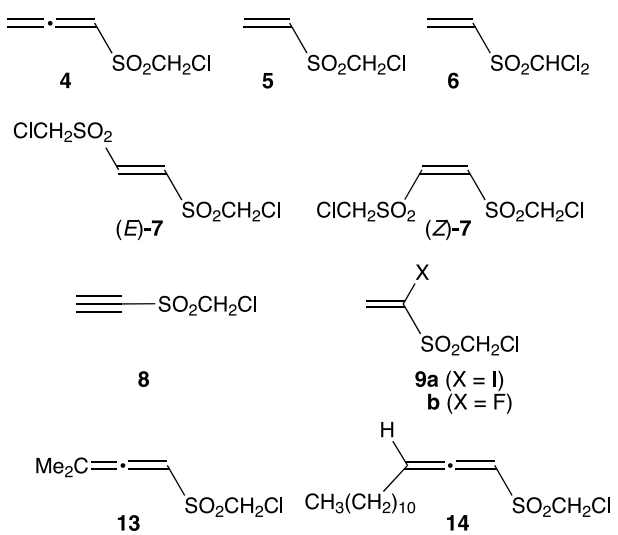
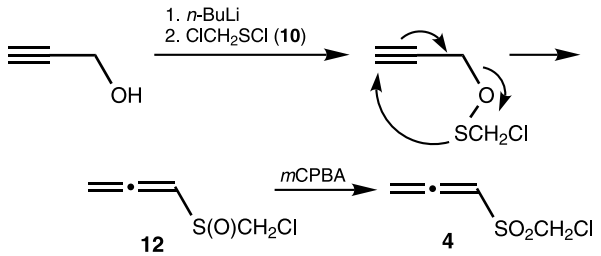


Figure 1. Potential prepackaged RB reagents.

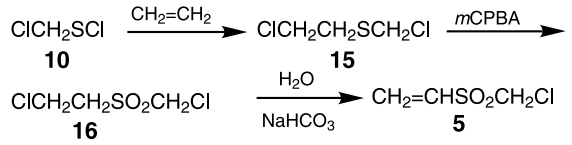
Compounds **4**-**9** should be powerful electron deficient Diels–Alder dienophiles as well as 1,3-dipolarophiles in 1,3-dipolar additions since it is known that sulfonyl groups, and in particular α-chloromethanesulfonyl groups, lower the level of the LUMO in such compounds.[9] It was anticipated that several of these compounds might also function as eneophiles in ene-reactions. Compound **9a** offers the possibility of replacing (by Stille/Heck type reactions) the iodine by sp^2- or sp-hybridized carbon functionalities, giving compounds which might find use in MIRB reactions, while **9b** could afford new fluoroolefins.

2.1.1. Synthesis of [(chloromethyl)sulfonyl]-1,2-propadienes 4 and homologues 13 and 14. It was anticipated that **4** could be prepared via a sequence involving coupling of chloromethanesulfenyl chloride ($ClCH_2SCl$, **10**) with propargyl alcohol giving *S*-chloromethyl propargyl sulfenate (**11**), [2,3]-sigmatropic rearrangement[10a] of **11** to [(chloromethyl)sulfinyl]-1,2-propadiene (**12**) and oxidation of **12** to **4** (Scheme 7). The success of our procedure depended in part on our discovery that Douglass' synthesis of **10** from the solid chlorination product of dimethyl disulfide, CH_3SCl_3,[10b] can be substantially improved if the latter is prepared and decomposed as a dilute solution in CH_2Cl_2. Under these conditions, pure **10** can be conveniently and safely prepared on a large scale in almost quantitative yield. Formation of the sulfenate ester is best conducted by reacting an ethereal solution of 1 equiv. of the lithium salt of the propargylic alcohol at −78 °C with **10** and then repeatedly filtering the mixture as it warms to remove LiCl (which otherwise catalyzes decomposition). Concentration affords **12**, which on oxidation (*m*CPBA) affords **4** as a low-melting, colorless solid.



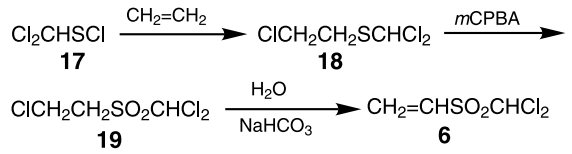
Scheme 7. Synthesis of reagent **4** from propargyl alcohol.

Commercially available 2-methyl-3-butyn-2-ol and tetradec-1-yn-3-ol (addition of ethynyl magnesium bromide[11] to dodecanal) were converted into 1-[(chloromethyl)sulfonyl]-3-methylbuta-1,2-diene ($Me_2C{=}C{=}CHSO_2CH_2Cl$, **13**) and [(chloromethyl)sulfonyl]-3-tetradeca-1,2-diene (CH_3-$(CH_2)_{10}CH{=}C{=}CHSO_2CH_2Cl$, **14**), respectively, by the method used to make **4**. Allenes **13** and **14** were less prone to decomposition than **4** and could be purified by column chromatography, although purification is not necessary as the crude compounds were at least 95% pure.



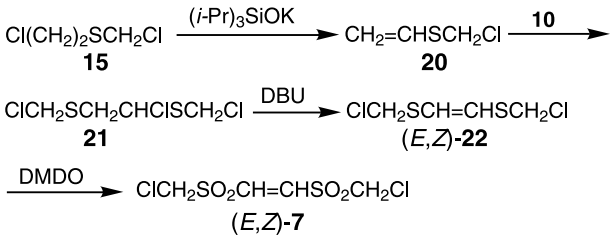
Scheme 8. Synthesis of reagent **5**.

2.1.2. Synthesis of [(chloromethyl)sulfonyl]ethene (5) and [(dichloromethyl)sulfonyl]ethene (6). Treatment of **10** with ethylene gives the known[12a] 1-chloro-2-[(chloromethyl)thio]ethane (**15**; 90%) which, without purification, is oxidized with 2 equiv. *m*CPBA (giving **16** (not isolated)) and stirred with aqueous $NaHCO_3$ giving **5** (99%), a colorless oil (Scheme 8). A similar sequence of steps can be used to convert Cl_2CHSCl (**17**; from chlorination of **10**)[10b] into **6** (78%) by way of 1-chloro-2-[(dichloromethyl)-thio]ethane (**18**) and 1-chloro-2-[(dichloromethyl)sulfonyl]-ethane (**19**), neither of which is isolated (Scheme 9).



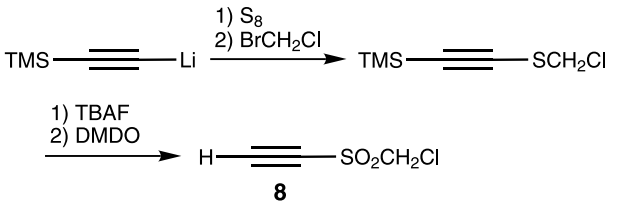
Scheme 9. Synthesis of reagent **6**.

2.1.3. Synthesis of (*E*/*Z*)-1,2-bis-[(chloromethyl)sulfonyl]-ethene ((*E*/*Z*)-7). Dehydrochlorination of **15** with $(i\text{-Pr})_3SiOK$[12b] gives [(chloromethyl)thio]ethene (**20**; 69%; Scheme 10). Compound **20** is converted into (*E*/*Z*)-1,2-bis-[(chloromethyl)sulfonyl]ethene ((*E*/*Z*)-**7**) by sequential addition of **10** (giving **21**; 96%), DBU dehydrochlorination of **21** to (*E*/*Z*)-**22** (58%; 1:3 *E*/*Z*), and oxidation with excess dimethyldioxirane (DMDO)[18b] (giving 28% (*E*)-**7** and 20% (*Z*)-**7**; Scheme 10).



Scheme 10. Synthesis of reagent **7**.

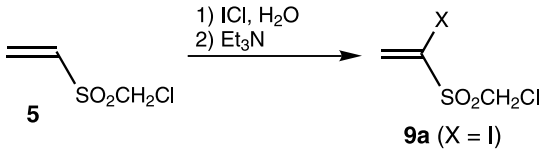
2.1.4. Synthesis of [(chloromethyl)sulfonyl]ethyne (8). Treatment of 2-(trimethylsilyl)ethynyllithium with sulfur followed by $BrCH_2Cl$ gave the known chloromethyl trimethylsilylethynyl sulfide, $TMSC{\equiv}CSCH_2Cl$.[13a,b] While this compound could be smoothly oxidized to the corresponding sulfone, efforts to desilylate this latter compound led to extensive decomposition. However, by reversing the sequence of reactions, namely by first desilylating and then oxidizing (2 equiv. DMDO), compound **8** could be directly prepared (Scheme 11). With less than 2 equiv. of DMDO, the corresponding sulfoxide, [(chloromethyl)sulfinyl]-ethyne, $HC{\equiv}CS(O)CH_2Cl$, was obtained instead of **8**. The series of compounds including the known[13a,b] $HC{\equiv}CSCH_2Cl$ and new $HC{\equiv}CS(O)CH_2Cl$ and $HC{\equiv}CSO_2CH_2Cl$ (**8**) showed interesting trends in their IR spectra, with ≡C–H at 3284, 3248 and 3242 cm^{-1}, and C≡C 2355/2332, 2050 and 2068 cm^{-1}, respectively, in



Scheme 11. Synthesis of **8** from the known 1-chloromethanesulfanyl-2-trimethylsilylethyne.

addition to the sulfoxide S=O at 1078 and the sulfone bands at 1343 and 1161 cm^{-1}.

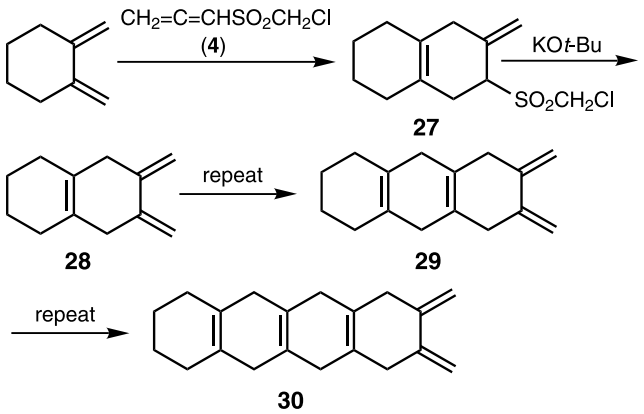
2.1.5. Synthesis of 1-iodo-1-[(chloromethyl)sulfonyl]-ethene (9a); attempted synthesis of 1-fluoro-1-[(chloromethyl)sulfonyl]ethene (9b). Treatment of aqueous solutions of **5** with iodine monochloride followed by triethylamine gave 1-iodo-1-[(chloromethyl)sulfonyl]ethene (**9a**) (Scheme 12). Efforts to prepare **9b** via addition of F_2 (as a 5% mixture with N_2)[13c] to **5** were unsuccessful.



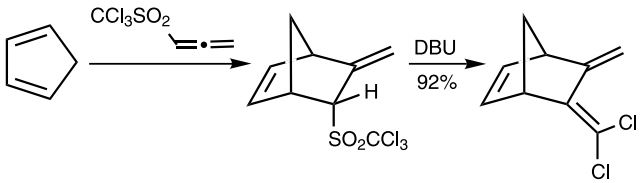
Scheme 12. Synthesis of **9a** from **5**.

2.2. Reactions of [(chloromethyl)sulfonyl]-1,2-propadienes

We examined the Diels–Alder reactivity of **4**, a potential 1,2,3-butatriene synthon. While (*Z*)-1,4-dichloro-2-butene may also be considered a 1,2,3-butatriene synthon, as a dienophile it requires "severe and carefully controlled reaction conditions [typically several days at 190–200 °C], was somewhat erratic", gave only moderate yields,



Scheme 13. Iterative cyclohomologation sequence using **4**.



Scheme 14. Tandem Diels–Alder RB reaction of [(trichloromethyl)sulfonyl]-1,2-propadiene.

Table 1. Tandem Diels–Alder Ramberg–Bäcklund products from compounds **4**–**6**, **13** and **14**

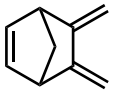
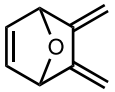
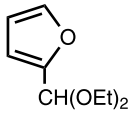
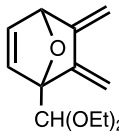
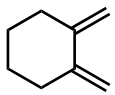
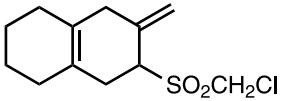
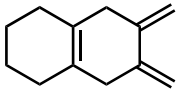
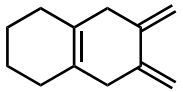
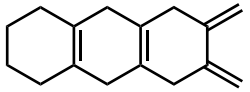
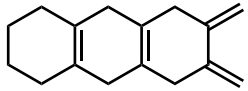
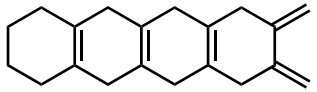
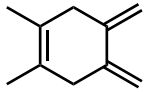
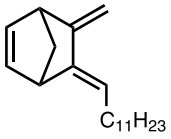
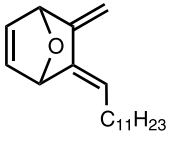
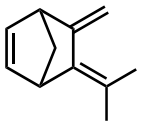
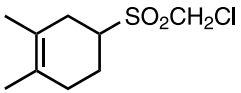
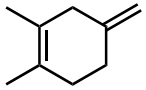
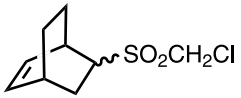
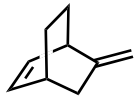
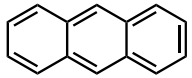
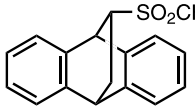
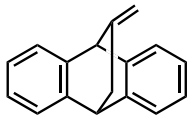
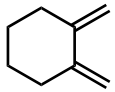
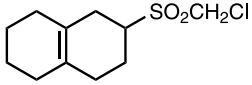
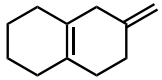
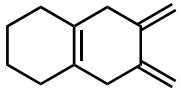
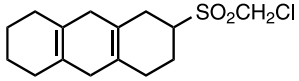
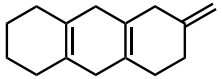
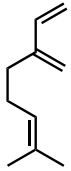
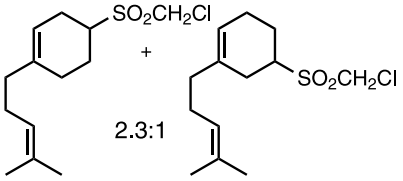
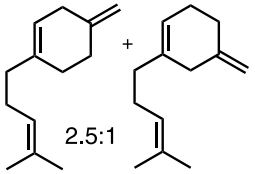
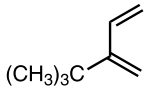
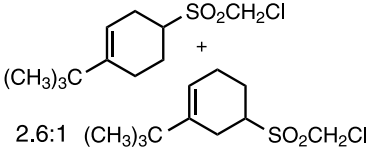
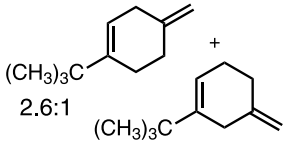
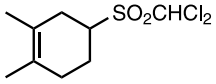
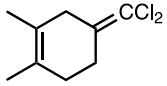
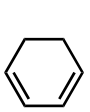
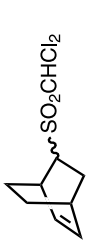
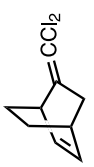
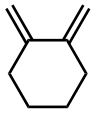
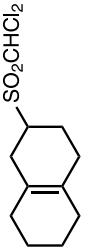
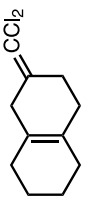
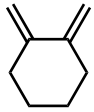
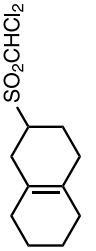
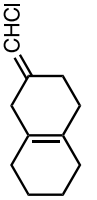
#	Diene	Dienophile	Diels–Alder adduct	Yield (%)	Ramberg–Bäcklund product	Yield (%)
1		**4**, 60 °C 30 min	—	—	 **23**	85
2		**4**, 60 °C 3 h	—	—	 **24**	85
3		**4**, 60 °C 2 h	—	—	 **25**	68
4		**4**, 60 °C 2 h	—	—	 **26**	60
5		**4**, 60 °C, 6 h	 **27**	76	 **28**	86
6	 **28**	**4**, 60 °C 3 h	—	—	 **29**	85
7	 **29**	**4**, 60 °C 3 h	—	—	 **30**	85
8		**4**, 80 °C 5 h	—	—	 **31**	57
9		**14**, 80 °C 5 h	—	—	 **32**	60
10		**14**, 80 °C 5 h	—	—	 **33**	49

Table 1 (*continued*)

#	Diene	Dienophile	Diels–Alder adduct		Yield (%)	Ramberg–Bäcklund product		Yield (%)
11		**13**, 80 °C 5 h	—		—		**34**	85
12		**5**, 120–130 °C 12 h		**35**	96		**36**	59[a]
13		**5**, 120–130 °C 12 h		**37**	95[b]		**38**	51[a]
14		**5**, 155 °C 7 h		**39**	96		**40**	89
15		**5**, 110 °C 16 h		**41**	97		**42**	79
16		**28** **5**, 60 °C 12 h		**43**	92		**44**	75
17		**5**, 145 °C 7 h			76			90
			45a	**45b**		**46a**	**46b**	
18		**5**, 150 °C 12 h		**47a** **47b**	74		**48a** **48b**	67
19		**6**, 80–100 °C 16 h		**50**	93		**51**	72[a]

(*continued on next page*)

Table 1 (*continued*)

#	Diene	Dienophile	Diels–Alder adduct	Yield (%)	Ramberg–Bäcklund product	Yield (%)
20		**6**, 80–100 °C 16 h	 **52**	92[c]	 **53**	72[a]
21		**6**, 80–100 °C 16 h	 **54**	94	 **55**	65[a]
22		**6**, 80–100 °C 16 h	 **54**	94	 **56**	55[d]

[a] 6.3:1 *endo*/*exo*.
[b] 3:1 *endo*/*exo*.
[c] $MeSO_2CCl_3$ (**49**) also required.
[d] Without **49**, **42** and **55** also formed (6% each).

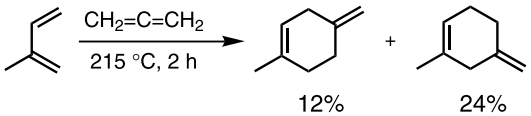
and does not react with either furan or 1,3-cyclohexadiene.[14]

When a 2:1 mixture of 1,2-bis(methylene)cyclohexane[2e,f] and **4** was warmed to 60 °C for 3 h and the product **27** (Scheme 13) was diluted with THF, treated with 1 equiv. of KO*t*-Bu at 0 °C, and worked up, triene **28** could be isolated in 57% overall yield via RB reaction of **27**. Repetition of the process twice gave tetraene **29** and then pentaene **30**, each in 85% overall yield. In these reactions **4** functions as a synthon for 1,2,3-butatriene. The sequence of reactions constitutes an iterative cyclohomologation approach to the synthesis of fused 1,4-cyclohexadienes. This protocol has been employed in syntheses of [*n*]beltenes.[15] Use of [(trichloromethyl)sulfonyl]-1,2-propadiene as a 1,1-dichloro-1,2,3-butatriene synthon has also been described (Scheme 14).[16a]

Table 1, entries 1–11, show the results of use of the above procedure with Diels–Alder adducts obtained from reaction of **4**, **13** and **14** with cyclopentadiene, furan, furfural diethyl acetal, 1,3-cyclohexadiene, 1,2-bis(methylene)cyclohexane, **28**, **29**, and 2,3-dimethyl-1,3-butadiene affording compounds **23**-**34**.

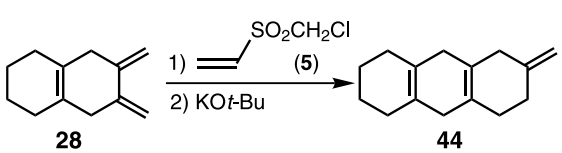
2.3. Reactions of [(chloromethyl)sulfonyl]ethene (5) and [(dichloromethyl)sulfonyl]ethene (6)

We examined the Diels–Alder reactivity of new compounds **5** and **6**, potential allene or chloroallene synthons. While Diels–Alder adducts of allene are useful synthetic intermediates, preparation of these compounds using allene itself is generally impractical because of its cost, low reactivity, lack of regioselectivity (Scheme 15) and the experimental difficulties associated with gaseous reagents.[16b] Because of the above problems, a variety of allene synthons have been devised, such as 1-bromo-1-(methylsulfonyl)ethene,[5] α-bromoacrolein,[17a] 2-(phenylsulfinyl)propene,[17b] ethenyl triphenylphosphonium bromide,[17c] α-methylene-β-propiolactone,[17d] and 1,2-[bis(phenylsulfonyl)]propene.[17e]

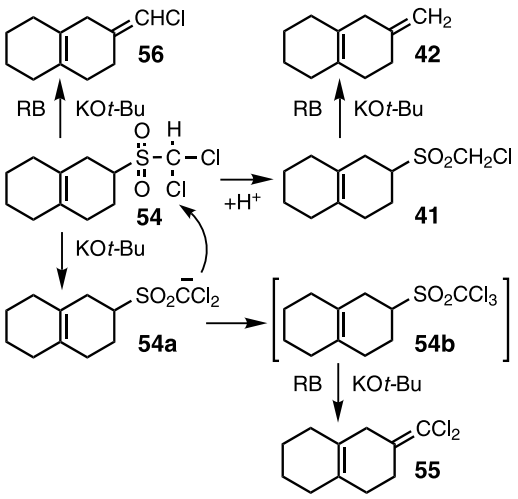


Scheme 15. Diels–Alder reaction of allene with isoprene.

Both **5** and **6** readily add to a variety of 1,3-dienes giving high yields of the corresponding Diels–Alder adducts, as shown in Table 1, entries 12–22, and Scheme 16. As anticipated, treatment of the Diels–Alder adducts of **5** with KO*t*-Bu/THF give good yields of the diene–allene adducts via Ramberg–Bäcklund reaction (entries 12–16). Analogous 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



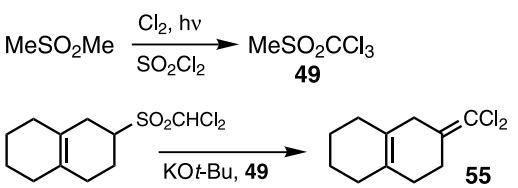
Scheme 16. Tandem Diels–Alder RB reaction of **5**.



Scheme 17. Proposed mechanism for the reaction of a Diels–Alder adduct of **6** with base.

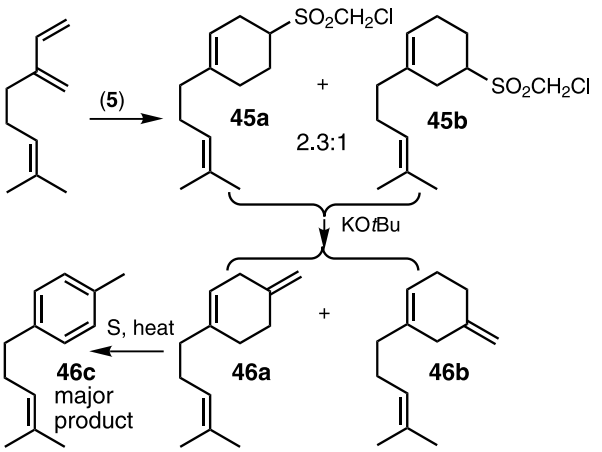
(**56**, **42**, **55**, respectively, Scheme 17). The latter two compounds are presumably formed by nucleophilic attack of the α-sulfonyl-α-chlorocarbanion **54a** of the Diels–Alder adduct **54** of **6** on the chlorine of a second adduct molecule giving [(trichloromethyl)sulfonyl]ethene adduct **54b**, which is not isolated.

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 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, $MeSO_2CCl_3$ (**49**), was used as a novel chlorine source. This little studied compound[18a] was conveniently prepared in 91% yield by bubbling Cl_2 into a refluxing, UV-irradiated solution of dimethyl sulfone in SO_2Cl_2 (Scheme 18). 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 2 equiv. of $MeSO_2CCl_3$, the corresponding Diels–Alder adducts of 1,1-dichloropropa-1,2-diene were formed in good yield (Table 1, entries 19–21), despite concerns about competing sulfonate formation sometimes seen in reactions involving base treatment of 1,1,1-trichloromethyl sulfones.[18c]



Scheme 18. Synthesis of [(trichloromethyl)sulfonyl]methane (**49**) and $CH_2{=}C{=}CCl_2$ Diels–Alder adduct **55**.

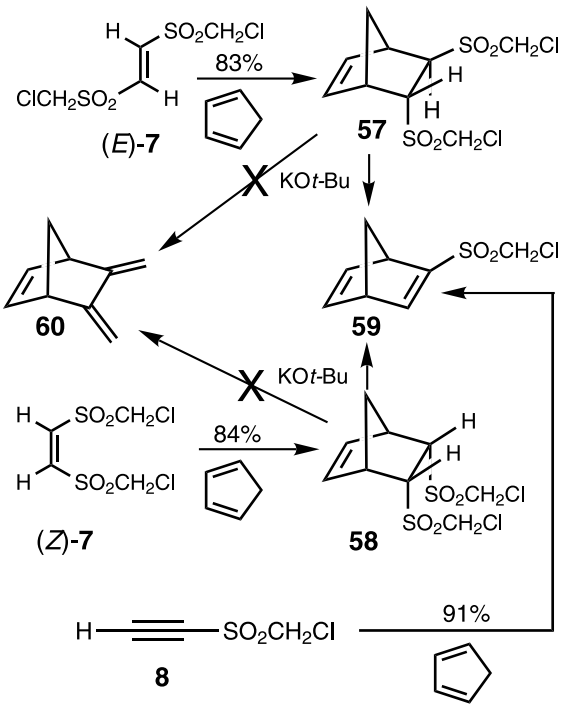
Mixtures of adducts were obtained on reaction of **5** or **6** with 2-substituted 1,3-dienes, for example, myrcene (76%; 2.3:1 *para*/*meta* mixture **45a**,**b** with **5**) and 2-*t*-butyl-1,3-butadiene (74%, 2.6:1 *para*/*meta* mixture **47a**,**b**). Individual adducts could not be separated chromatographically from the isomeric mixtures. Treatment of the mixtures of adducts with base afforded isomeric allene adducts **46a**,**b** and **48a**,**b** of myrcene and 2-*t*-butyl-1,3-butadiene, respectively. In the former case heating the **46a**,**b** mixture with sulfur let to aromatization affording 4-methyl-1-(4′methylpent-3′-enyl)-benzene **46c** as the major product, which in turn suggests that the *para* adduct **45a** of **5** with myrcene was the predominant adduct (Scheme 19).



Scheme 19. Reaction of **5** with myrcene, a 2-substituted 1,3-butadiene, gives a mixture of adducts.

2.4. Reactions of (*E*/*Z*)-1,2-bis-[(chloromethyl)sulfonyl]-ethene (7a/7b)

Both (*E*)- and (*Z*)-**7** readily form Diels–Alder adducts, for example, **57** and **58**, respectively, with 1,3-cyclopentadiene (Scheme 20), as confirmed by X-ray crystallography for **57**,[3] which also establishes the stereochemistry of (*E*)-**7**. The X-ray structure of **57** shows SCCS and HCCH (the two sulfur-bonded ring carbons) dihedral angles of −110.58(16)° and 124(3)°. Similarly, *cis* isomer **58** should

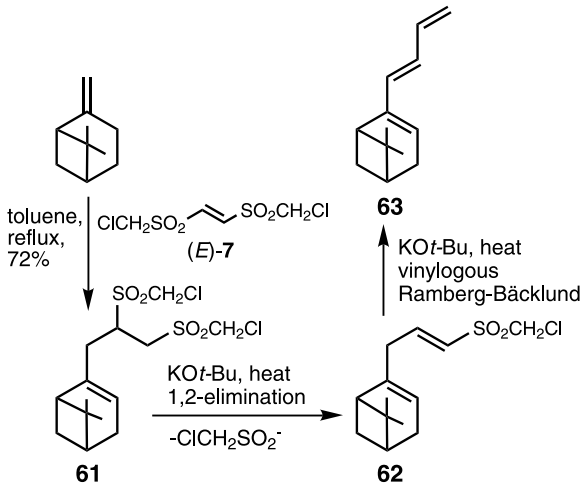


Scheme 20. Reaction of **57** and **58** with base; alternative synthesis of **59** via Diels–Alder addition of **8**.

have H on C(26) or C(27) far from *syn* or *anti*-periplanar with sulfur.

Base treatment of **57** or **58** gave unstable 2-[(chloromethyl)-sulfonyl]bicyclo[2.2.1]hepta-2,5-diene (**59**) rather than 5,6-bis(methylene)bicyclo[2.2.1]hept-2-ene (**60**), for example, 1,2-elimination from the activated α-sulfonyl carbanions is favored over 1,3-elimination (Ramberg–Bäcklund reaction), even with the adduct of (*Z*)-**7**, where a coplanar 1,2-elimination transition state is impossible. Compound **59** could be directly prepared in high yield from Diels–Alder addition of [(chloromethyl)sulfonyl]-ethyne (**8**) to cyclopentadiene (Scheme 20).

Since compound **7** showed good reactivity as a dienophile, we examined its reactivity in the ene reaction. When (*E*)-**7** was heated with 2 equiv. of β-pinene in toluene at 135 °C for 1.5 h, the ene product 2-{[(1′,2′-bis(chloromethyl)sulfo-nyl]propyl}-6,6-dimethylbicyclo[3.1.1]hept-2-ene (**61**) was formed in 72% yield as a crystalline solid. Base treatment (KO*t*-Bu) of **61** in refluxing THF afforded (*E*)-2-(buta-1,3-dienyl)-6,6-dimethylbicyclo[3.3.1]hept-2ene (**63**) in low yield. If treatment with base was conducted at 0 °C, low yields of 2-[(3-chloromethyl)sulfonyl]allyl-6,6-dimethyl-bicyclo[3.3.1]hept-2-ene (**62**) could be isolated, leading to the overall proposed mechanism shown in Scheme 21. While not of synthetic utility due to low yield, the reaction in Scheme 21 represents the first example of a tandem reaction sequence incorporating an ene-reaction with Ramberg–Bäcklund elimination.



Scheme 21. Ene-reaction of (*E*)-**7** with β-pinene followed by RB reaction of β-elimination product **62**.

Efforts to use easily prepared **8** as an eneophile with β-pinene did not appear to be promising due to the thermal instability of **8**. In addition, efforts to replace the iodine atom of **9a** with sp^2- or sp-hybridized carbon groups through Pd(0)-catalyzed reactions have not been successful thus far.

3. Conclusion

We have demonstrated that [(chloromethyl)sulfonyl]-1,3-propadiene (**4**), [(chloromethyl)sulfonyl]ethene (**5**), and [(dichloromethyl)sulfonyl]ethene (**6**) are new, easily prepared reagents which have considerable utility as pre-packaged Ramberg–Bäcklund reagents. When combined with Diels–Alder addition, these compounds conveniently afford in good yields the formal adducts of 1,2,3-butatriene (from **4**), allene (from **5**) and 1,1-dichloroallene (from **6**; when used in conjunction with a chlorine source such as [(trichloromethyl)sulfonyl]methane) **49**.

4. Experimental

4.1. Caution

β-Chlorosulfides may be toxic on inhalation, ingestion or skin contact. These compounds should only be handled in a well-ventilated hood using rubber gloves. All glassware used should be rinsed with bleach (‘Clorox’) immediately after use.

4.2. General methods

Reaction flasks were oven dried and cooled under nitrogen. Diethyl ether and THF were distilled from sodium-benzophenone ketyl; CH_2Cl_2 was distilled from CaH_2. Propargyl alcohol was distilled prior to use. Unless otherwise noted, silica gel (Fisher Scientific Co., 200–425 mesh, 60 Å) was used as the chromatography solid phase and solutions were dried over anhydrous $MgSO_4$. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini at 300 and 75.1 MHz, respectively, in $CDCl_3$ unless otherwise noted, with all shifts referenced to TMS in ppm. IR spectra were recorded on a Perkin Elmer model 1600 FTIR or a Perkin Elmer 710B spectrophotometer. LR GC–MS was performed on a Hewlett Packard 5890 GC coupled to a Hewlett Packard 5970 MS (EI at 70 eV). Melting points were determined on a Buchi model 510 melting point apparatus and are uncorrected.

4.2.1. Chloromethanesulfenyl chloride (10). A magnetic stirrer-equipped flask was charged with CH_2Cl_2 (60 mL) and Me_2S_2 (9.16 g, 97 mmol), the mixture was cooled to −78 °C and Cl_2 gas was bubbled through slowly using a 9 mm glass tube (a solid was formed plugging smaller bore tubes). The mixture turned red-orange and a colorless solid (CH_3SCl_3) appeared. The mixture turned into a milky, yellow-white slurry, which continued to thicken and lighten until the solution became saturated with chlorine, at which time the mixture took on a yellow-green color. Addition of Cl_2 was stopped and a reflux condenser with drying tube was fitted to the flask. Decomposition of CH_3SCl_3 was promoted by warming the flask to room temperature. An orange liquid formed as HCl was evolved. Concentration in vacuo yielded the known **10**[10b] as a malodorous, lachrymatory oil (20 g, 88%) which was used without further purification; ^1H NMR δ 5.12 (s); ^{13}C NMR δ 54.8. If desired, **10** can be purified by distillation (bp 50–55 °C/115 mm).

4.2.2. 1-[(Chloromethyl)sulfonyl]-1,2-propadiene (4). To a solution of propargyl alcohol (4.8 mL, 80 mmol) in ether (240 mL) was added *n*-BuLi (2.5 M, 32 mL, 80 mmol, hexane) at −78 °C. The resultant thick colorless suspension was stirred for 20 min. Neat $ClCH_2SCl$ (**10**; 6.6 mL) was

added dropwise during 10 min. The mixture was stirred at −78 °C for 30 min, LiCl was removed by vacuum filtration through a silica gel pad, and the light yellow solution was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (80 mL). A solution of *m*-CPBA (77%, 26 g) in CH_2Cl_2 (200 mL) was added and the mixture was stirred at room temperature for 16 h. The colorless precipitate was removed by filtration, the filtrate was concentrated, and the residue was chromatographed (silica gel; 1:5 EtOAc/hexane) affording **4** as an oil or low melting solid, mp 39–39.5 °C (7.2 g, 59%); ^{1}H NMR δ 6.26 (t, J=6.3 Hz, 1H), 5.62 (d, J=6.3 Hz, 2H), 4.53 (s, 2H); ^{13}C NMR δ 212.3 (=C=), 95.2 (=CH), 84.3 (=CH_2), 58.3 (CH_2); IR 3000 (m), 1965 (m), 1328 (s), 1247 (m), 1148 (s), 1120 (s), 872 (m) cm^{-1}. EI HRMS calcd for $C_4H_5SO_2Cl$: 151.9698. Found: 151.9695. It is best to immediately oxidize the unstable intermediate **12**, which can be isolated, purified and characterized as colorless needles, mp 49–49.5 °C from ether/hexanes; ^{1}H NMR δ 6.00 (t, J=6 Hz, 1H), 5.30 (d, J=6 Hz, 2H), 4.40 (s, 2H); IR 3000 (m), 1925 (m), 1060 (s) cm^{-1}. It is also best to promptly purify the crude **4** by chromatography.

4.2.3. 1-[(Chloromethyl)sulfonyl]-3-methylbuta-1,2-diene (13). A 250 mL three-necked flask under N_2 was charged with diethyl ether (100 mL) and 2-methyl-3-butyn-2-ol (1 g, 11.9 mmol). The solution was cooled to −78 °C and *n*-BuLi (2.5 M, 4.76 mL, 11.9 mmol) was added dropwise. After 15 min **10** (1.38 g, 11.9 mmol) was added dropwise and the solution was stirred for 15 min. The solution was then continuously vacuum filtered as it warmed to room temperature. A sample of the product was concentrated in vacuo and analyzed: ^{1}H NMR δ 5.90 (m, 1H), 4.35 (m, 2H), 1.83 (m, 6H); ^{13}C NMR δ 203.4 (C), 105.5 (C), 95.5 (CH), 58.2 (CH_2), 20.0 (CH_3), 19.8 (CH_3); IR (ν_{max}) 3000 (s), 1950 (m), 1060 (vs) cm^{-1}. To the pale yellow solution was added CH_2Cl_2 (50 mL) and *m*-CPBA (50–60%) (3.75 g, 11.9 mmol). The solution was stirred overnight protected with a drying tube. The solution was then washed with saturated aqueous $NaHSO_3$ and $NaHCO_3$ (3× each). The organic layer was separated, dried and concentrated in vacuo to give **13** (1.31 g, 61%), a colorless oil: ^{1}H NMR δ 5.98 (m, 1H), 4.46 (s, 2H), 1.89 (d, J= 3.3 Hz, 3H); ^{13}C NMR δ 207.5 (C), 107.3 (C), 92.6 (CH), 57.7 (CH_2), 19.5 (CH_3); IR (ν_{max}) 3015 (m), 2950 (m), 1960 (m), 1320 (vs), 1115 (vs) cm^{-1}; mp ca. 10 °C; EI HRMS calcd for $C_6H_9SO_2Cl$: 180.0012. Found: 180.0018.

4.2.4. [(Chloromethyl)sulfonyl]-3-tetradeca-1,2-diene (14). A 250 mL three-necked flask under N_2 was charged with diethyl ether (100 mL) and tetradec-1-yn-3-ol (2 g, 9.5 mmol). The flask was cooled to −78 °C and *n*-BuLi (2.5 M, 3.8 mL, 9.5 mmol) was added dropwise. After 10 min **10** (1.1 g, 9.5 mmol) was added slowly with stirring. Workup and overnight oxidation (*m*-CPBA; 1.6 g, 9.5 mmol) as for **4** gave a yellow oil. Chromatography (5:1 CH_2Cl_2/hexane) gave **14** (2 g, 69% yield), a colorless low melting solid: mp 37 °C; ^{1}H NMR δ 6.15 (m, 1H), 5.99 (m, 1H), 4.48 (s, 2H), 2.23 (m, 2H), 1.47 (m, 2H), 1.24 (br s, 16H), 0.86 (t, J=7 Hz, 3H); ^{13}C NMR δ 208.9 (C), 101.3 (CH), 95.1 (CH), 57.9, 31.9, 29.5, 29.5, 29.4, 29.3, 29.3, 28.9, 28.4, 27.7, 22.7 (all CH_2), 14.1 (CH_3); IR (ν_{max}) 2924 (vs), 2853 (vs), 1954 (m), 1465 (m), 1330 (s), 1147 (s) cm^{-1}; EI HRMS calcd for $C_{14}H_{27}SO_2Cl$: 306.1420. Found: 306.1425.

4.2.5. 1-Chloro-2-[(chloromethyl)thio]ethane (15). A solution of $ClCH_2SCl$ (**10**; 19.2 g, 17.8 mmol) in CH_2Cl_2 (200 mL) was placed in a flask fitted with a gas inlet tube and a drying tube. Ethylene gas was slowly introduced at 0 °C until the starting material disappeared as indicated by ^{1}H NMR analysis. Concentration in vacuo afforded the known[12] **15** as a yellow oil (21.4 g, 90%) which was used directly for the next step without further purification; bp 99–100 °C (15 mm); ^{1}H NMR δ 4.75 (s, 2H), 3.76 (t, J=7.8 Hz, 2H), 3.11 (t, J=7.8 Hz, 2H); ^{13}C NMR δ 49.2, 42.4, 34.0; GC–MS *m/z* 146 (M^+, ^{37}Cl, 14%), 144 (M^+, ^{35}Cl, 20%), 111 (23%), 109 (63%), 95 (51%), 45 (100%).

4.2.6. [(Chloromethyl)sulfonyl]ethene (5). *m*-Chloroperbenzoic acid (77%, 107 g, 0.47 mol) was added to a solution of **15** (30.8 g, 0.21 mol) in CH_2Cl_2 (750 mL) over 30 min at room temperature and the mixture was stirred for 16 h. The colorless precipitate was removed by filtration and excess aqueous $NaHCO_3$ was added to the filtrate which was stirred for 16 h. The reaction mixture was washed with H_2O (3×200 mL) and brine (3×200 mL), and the organic phase was separated, dried (Na_2SO_4) and concentrated in vacuo affording **5** as a colorless oil (29.4 g, 99%); ^{1}H NMR δ 6.69 (dd, J=9.7, 16.6 Hz, 1H), 6.50 (d, J=16.6 Hz, 1H), 6.31 (d, J=9.7 Hz, 1H), 4.43 (s, 2H); ^{13}C NMR δ 56.6, 132.8, 134.1; IR ($CHCl_3$) 1149, 1325 (SO_2) cm^{-1}.

4.2.7. 1-Chloro-2-[(dichloromethyl)thio]ethane (18). A three-necked round bottom flask was charged with Me_2S_2 (10 mL, 113 mmol) and CH_2Cl_2 (120 mL). The solution was cooled to −78 °C and Cl_2 gas was bubbled through slowly for 3–5 min. The reaction mixture turned reddish orange and a colorless solid precipitated (CH_3SCl_3). The slurry continued to thicken until the solution had been saturated with Cl_2, at which time the mixture took on a yellow-green color and the addition of Cl_2 was stopped. The reaction mixture was warmed to room temperature and stirred for 1 h to give a bright orange solution with the release of HCl gas, which was absorbed with aqueous NaOH solution. The orange solution was cooled to −78 °C and Cl_2 gas was bubbled through again. As before, a colorless solid precipitated. The slurry continued to thicken until the solution had been saturated with Cl_2, at which time the mixture took on a yellow-green color and the addition of Cl_2 was stopped. The reaction mixture was warmed to room temperature, stirred for 1 h, concentrated in vacuo and diluted with CH_2Cl_2 (300 mL). The solution was cooled to 0 °C and ethylene gas was bubbled in through a glass tube until the color of the solution lightened. Concentration in vacuo afforded **18** as a yellow oil (37.2 g; 91%). The product was used directly for the next step without further purification; ^{1}H NMR δ 6.83 (s, 1H), 3.84 (t, J=7.3 Hz, 2H), 3.33 (t, J=7.3 Hz, 2H); ^{13}C NMR δ 73.9, 42.5, 34.1.

4.2.8. [(Dichloromethyl)sulfonyl]ethene (6). *m*-Chloroperbenzoic acid (77%, 27 g, 120 mmol) was added to a solution of **18** (9.0 g, 50 mol) in CH_2Cl_2 (200 mL) over 30 min at 20 °C and the mixture was stirred for 16 h. The colorless precipitate was removed by filtration. The filtrate was concentrated and the residue chromatographed (silica gel;

6:1 hexane/EtOAc). The so-purified **19** was dissolved in CH_2Cl_2 (200 mL), mixed with 1.1 equiv. of aqueous $NaHCO_3$ (excess $NaHCO_3$ is detrimental) and stirred for 16 h. The mixture was washed with H_2O (2×100 mL) and brine (2×100 mL), dried (Na_2SO_4), concentrated in vacuo, and chromatographed (5:1 hexane/EtOAc) to afford **6** as a low melting solid, mp 50–51 °C (7.5 g, 86%): ^{1}H NMR δ 6.86 (dd, J=9.8, 16.6 Hz, 1H), 6.69 (d, J=16.6 Hz, 1H), 6.55 (d, J=9.8 Hz, 1H), 6.26 (s, 1H); ^{13}C NMR δ 78.7, 129.8, 137.3; IR ($CHCl_3$) 1145, 1348 (SO_2), 948, 3020 cm^{-1} (C═C). Anal. Calcd for $C_3H_4Cl_2O_2S$: C, 20.59; H, 2.30. Found: C, 20.46; H, 2.07.

4.2.9. [(Chloromethyl)thio]ethene (20). Triisopropylsilanol (0.1 mL, 0.5 mmol) was added to a slurry of pulverized KOH (6.93 g, 0.12 mol) in tetraethyleneglycol dimethyl ether (150 mL) and the mixture was stirred at room temperature for 1 h. Compound **15** (2.91 g, 59 mmol) was added to the mixture and the color changed from yellow to dark brown. The mixture was stirred at 20 °C until the starting material had disappeared as indicated by TLC (7:1 hexane/EtOAc, ca. 1.5 h). The mixture was then distilled into a liquid nitrogen cooled trap (0.02 Torr). Compound **20** was separated as a colorless oil from the colorless precipitate using a syringe (4.38 g, 69%): ^{1}H NMR δ 6.39 (dd, J=10, 17 Hz, 1H), 5.40 (dd, J=2.4, 10 Hz, 1H), 5.39 (dd, J=2.4, 17 Hz, 1H), 4.78 (s, 2H); ^{13}C NMR δ 129.0, 115.4, 47.8; GC–MS m/z 110 (M^+, ^{37}Cl, 9%), 108 (M^+, ^{35}Cl, 27%), 73 (88%), 46 (27%), 45 (100%).

4.2.10. 1-Chloro-1,2-bis[(chloromethyl)thio]ethane (21). Compound **20** (3.03 g, 28 mmol) was added to $ClCH_2SCl$ (3.28 g, 28 mmol) in CH_2Cl_2 (50 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and concentrated in vacuo affording the title compound as a yellow oil (5.78 g, 96%). The product was used directly without further purification; ^{1}H NMR δ 5.53 (t, J=7 Hz, 1H), 4.98 and 4.80 (AB_q, J=11 Hz, 2H), 4.78 (s, 2H), 3.41 (d, J=7 Hz, 2H); ^{13}C NMR: δ 64.4, 49.3, 46.7, 38.9; GC–MS m/z 227 (M^+, ^{37}Cl, 10%), 225 (M^+, ^{35}Cl, 29%), 108 (94%), 97 (43%), 95 (100%).

4.2.11. (*E*,*Z*)-1,2-Bis[(chloromethyl)thio]ethene ((*E*,*Z*)-22). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 1.66 mL, 11 mmol) was added to a solution of **21** (1.42 g, 5.5 mmol) in $CHCl_3$ (50 mL) at 0 °C and the reaction mixture was heated to reflux for 1 h. The reaction progress was monitored by GC. The organic layer was washed with 0.5 N HCl (2×25 mL), $NaHCO_3$ solution (2×25 mL), brine (2×25 mL), dried (Na_2SO_4) and concentrated in vacuo. Distillation gave (*E*,*Z*)-**22** as a light yellow oil (0.61 g, 58%; *E*/*Z* 1.3:1), bp 90–100 °C (0.02 Torr); ^{1}H NMR. δ 6.48 (s, 2H), 6.46 (s, 2H), 4.76 (s, 8H); ^{13}C NMR δ 124.1, 123.5, 48.7, 48.5; GC–MS m/z 190 (M^+, ^{37}Cl, 33%), 190 (M^+, ^{35}Cl, 45%), 106 (93%), 104 (100%), 103 (70%).

4.2.12. (*E*,*Z*)-1,2-Bis[(chloromethyl)sulfonyl]ethene ((*E*,*Z*)-7). Dimethyldioxirane[18b] (DMDO; 100 mL, 9.0 mmol) was added to a solution of **22** (0.4 g, 2.1 mmol) in $CHCl_3$ (5 mL) at room temperature and the reaction mixture was stirred at room temperature overnight. The resulting mixture was dried (Na_2SO_4), concentrated in vacuo, and the residue chromatographed (hexanes/EtOAc 3:2) affording both the (*E*)-**7** (R_f 0.8, 0.15 g, 28%) and the (*Z*)-**7** (R_f 0.6, 0.11 g, 20%) as colorless solids: (*E*)-**7**, mp 143–145 °C (EtOH); IR (film) 1389 (SO_2), 1124 (SO_2) cm^{-1}; ^{1}H NMR ($CD_3C(O)CD_3$) δ 7.82 (s, 2H), 5.22 (s, 4H); ^{13}C NMR ($CD_3C(O)CD_3$) δ 141.9, 57.2. Anal. Calcd for $C_4H_6Cl_2O_4S_2$: C, 18.98; H, 2.39. Found: C, 19.37; H, 2.06. (*Z*)-**7**, mp 113–115 °C (EtOH); IR (film) 1329 (SO_2), 1119 (SO_2) cm^{-1}; ^{1}H NMR ($CD_3C(O)CD_3$) δ 7.60 (s, 2H), 5.17 (s, 4H); ^{13}C NMR ($CD_3C(O)CD_3$) δ 141.8, 58.8.

4.2.13. [(Chloromethyl)sulfonyl]ethyne (8). A solution of 1-(chloromethyl)thio-2-(trimethylsilyl)ethyne (1.5 g, 8.4 mmol)[13a] in methanol (2 mL) at 0 °C was treated dropwise with Bu_4NF (3.75 mL, 9.2 mmol; 75% aqueous solution). The mixture was stirred at 0 °C for 2 h, and then diluted with ice water and extracted with pentane. The extracts were washed with cold water, dried (Na_2SO_4), cooled to 0 °C, and treated overnight with a solution of DMDO in acetone (18 mmol, 200 mL, 9 mmol/100 mL). Solvents were removed in vacuo and the residue was chromatographed (6:1 hexane/ethyl acetate), yielding the title compound (0.7 g, 60%) as a colorless oil: ^{1}H NMR δ 4.60 (s, 2H); 3.60 (s, 1H); ^{13}C NMR δ 91.7, 78.8, 60.6; IR (neat) 3242 (triple bond C–H), 1342, 1159 cm^{-1} (SO_2).

4.2.14. 1-[(Chloromethyl)sulfonyl]-1-iodoethene (9a). To a solution of **5** (1.41 g, 10 mmol) in 1:1 THF and water (30 mL) was added iodine monochloride (3.25 g, 20 mmol) at room temperature. The mixture was stirred overnight, concentrated in vacuo, the residue was extracted with CH_2Cl_2 (20×2 mL) and washed with aqueous sodium thiosulfate solution (20 mL) giving 2-chloro-1-[(chloromethyl)sulfonyl]-1-iodoethane (1.2 g, 40%). A portion of this latter compound (1.00 g, 3.3 mmol) in THF (15 mL) was treated with triethylamine (3 mL) which was added dropwise at room temperature. The mixture was stirred for 20 min, quenched with dilute HCl, extracted with CH_2Cl_2 (30×2 mL), dried, concentrated in vacuo and the residue chromatographed (5:1 hexane/ethyl acetate) to yield **9a** (862 mg, 89%) as colorless crystals, mp 49–50 °C; ^{1}H NMR δ 7.55 (d, J=2.9 Hz, 1H), 6.81 (d, J=2.9 Hz, 1H), 4.61 (s, 2H); ^{13}C NMR δ 144.1, 95.6, 52.6; IR (CH_2Cl_2) 1331, 1155 cm^{-1} (SO_2); EI-MS m/z 266 (M^+, 28%), 152 (100%), 126 (56%). Anal. Calcd for $C_3H_4ClIO_2S$: C, 13.52; H, 1.51. Found: C, 13.93; 2.53.

4.2.15. 5,6-Bis(methylene)bicyclo[2.2.1]hept-2-ene (23) [Table 1, entry 1]. A 2 mL screw capped vial was charged with **4** (0.5 g, 3.3 mmol), freshly distilled cyclopentadiene (0.65 g, 9.9 mmol), sealed and held at 60 °C. By GC, the reaction was found to be complete in 30 min (GC–MS m/z 218 (M^+, 0.77%), 105 (100%), 103 (25%), 79 (50%), 77 (42%), 39 (23%)). The product was placed in a 50 mL flask, dissolved in THF (10 mL) under N_2, cooled to 0 °C and a solution of KO*t*-Bu (0.57 g, 3.3 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 15 min and quenched with saturated aqueous NH_4Cl. Diethyl ether (10 mL) was added and the organic layer was removed, dried, and concentrated in vacuo. Chromatography (pentane) gave known compound **23**[14a,19] slightly contaminated with dicyclopentadiene (0.32 g, 85%): ^{13}C NMR δ 149.1 (C), 132.1 (CH), 101.2 (CH_2), 51.2 (CH), 50.3 (CH_2); GC–

MS *m/z* 118 (M^+, 54%), 117 (97%), 91 (40%), 66 (100%), 65 (36%), 51 (44%), 50 (29%), 39 (75%).

4.2.16. 5,6-Bis(methylene)-7-oxabicyclo[2.2.1]hept-2-ene (24) [Table 1, entry 2]. A 2 mL screw capped vial was charged with **4** (0.5 g, 3.3 mmol), furan (0.67 g, 9.9 mmol), sealed and maintained at 60 °C. The reaction was complete in 3 h according to GC analysis. The product was placed in a 50 mL flask, dissolved in THF (10 mL) under N_2, cooled to 0 °C and a solution of KO*t*-Bu (0.57 g, 3.3 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 15 min and quenched with saturated aqueous NH_4Cl. Diethyl ether (10 mL) was added, and the organic layer was separated, dried, concentrated in vacuo and chromatographed (pentane) giving known **24**[20] (0.34 g, 85%) as a colorless oil: ^{1}H NMR δ 6.74 (br s, 2H), 5.28 (br s, 2H), 5.16 (br s, 2H), 5.12 (br s, 2H); ^{13}C NMR δ 143.2 (C), 135.6 (CH), 102.6 (CH_2), 82.8 (CH); GC–MS *m/z* 120 (M^+, 2%), 92 (16%), 91 (100%), 68 (63%), 65 (36%), 63 (15%), 52 (28%), 51 (26%), 50 (19%), 39 (54%); EI HRMS calcd for C_8H_8O: 120.0575. Found: 120.0569.

4.2.17. 5,6-Bis(methylene)-7-oxabicyclo[2.2.1]hept-2-ene-1-carboxaldehyde diethylacetal (25) [Table 1, entry 3]. A 2 mL screw capped vial was charged with **4** (0.5 g, 3.3 mmol), 2-(bis(ethoxy)methyl) furan (1.2 g, 7.1 mmol) and sealed. The mixture was heated for 2 h at 60 °C. A 25 mL three-necked flask was charged with the product in THF (5 mL) under N_2. The flask was cooled to 0 °C and a solution of KO*t*-Bu (0.37 g, 3.3 mmol) in THF (5 mL) was added dropwise. The deep red solution was stirred for 15 min, quenched with saturated aqueous NH_4Cl, and the organic layer was separated, dried and concentrated in vacuo to yield a pale yellow oil. Chromatography (CH_2Cl_2/hexane (5:1)) gave **25** (0.5 g; 68%) as a colorless oil: ^{1}H NMR δ 6.51 (d, *J*=5.1 Hz, 1H), 6.34 (dd, *J*=5.1, 2.8 Hz, 1H), 5.34 (s, 1H), 5.24 (s, 1H), 5.16 (br s, 1H), 5.06 (s, 1H), 4.97 (s, 1H) 3.91 (m, 1H), 3.73 (m, 3H), 1.29 (t, *J*=6.7 Hz, 3H), 1.24 (t, *J*=6.7 Hz, 3H); ^{13}C NMR δ 150.1, 143.2 (both C), 135.6, 135.5, 103.0 (all CH), 101.7, 100.4 (both CH_2), 82.2, 71.7 (both CH), 63.9, 63.7 (both CH_2), 15.4, 15.3 (both CH_3); GC–MS *m/z* 222 (M^+, 0.1%), 125 (17%), 103 (50%), 97 (20%), 91 (30%), 75 (52%), 65 (19%), 47 (100%), 39 (23%); EI HRMS calcd for $C_{13}H_{18}O_3$: 222.1256. Found: 222.1253.

4.2.18. 5,6-Bis(methylene)bicyclo[2.2.2]oct-2-ene (26) [Table 1, entry 4]. A 2 mL screw capped vial, charged with **4** (0.5 g, 3.3 mmol) and 1,3-cyclohexadiene (0.79 g, 9.9 mmol) was sealed and kept at 60 °C. The reaction was complete in 2 h as determined by GC. The reaction gave two products in a 3:1 ratio: GC–MS *m/z* 232 (M^+, 0.06%), 119 (26%), 91 (100%), 65 (18%), 51 (8%), 41 (11%), 39 (13%). The products were placed in a 50 mL flask, dissolved in THF (10 mL) under N_2, cooled to 0 °C and a solution of KO*t*-Bu (0.57 g, 3.3 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 15 min and quenched with saturated aqueous NH_4Cl. Diethyl ether (10 mL) was added and the organic layer was separated, dried, concentrated in vacuo, and chromatographed (pentane) giving known **26**[14a,19] (0.26 g, 60%) as a colorless oil: ^{1}H NMR δ 6.2 (m, 2H), 5.1 (s, 2H), 4.7 (s, 2H), 3.2 (m, 2H), 1.6 (m, 2H), 1.4 (m, 2H); ^{13}C NMR δ 147.1 (C), 133.3 (CH), 102.2 (CH_2), 42.3 (CH), 26.1 (CH_2); GC–MS, *m/z* 132 (M^+, 11%), 105 (9%), 104 (100%), 91 (9%), 78 (34%), 77 (17%), 51 (18%), 50 (9%), 39 (20%).

4.2.19. 2-[(Chloromethyl)sulfonyl]-3-methylene-1,2,3,4,5,6,7,8-octahydronaphthalene (27) [Table 1, entry 5]. A 100 mL round-bottomed flask fitted with a reflux condenser was charged with 1,2-bis(methylene)cyclohexane (2.16 g, 20 mmol) and **4** (6.1 g, 40 mmol) under argon. The mixture was heated to 60 °C, stirred for 6 h, concentrated in vacuo, and chromatographed (6:1 hexane/EtOAc) giving **27** (3.95 g, 76%) as a colorless oil; ^{1}H NMR δ 5.23 (d, *J*=3.1 Hz, 2H); 4.48 (dd, *J*=12.6, 144 Hz, 2H), 2.90 (dd, *J*=18.9, 113 Hz, 2H), 2.40–2.65 (m, 2H), 1.73–2.00 (m, 4H), 1.41–1.73 (m, 4H); ^{13}C NMR δ 137.7, 127.1, 123.6, 117.3, 60.3, 52.3, 35.4, 29.6, 29.3, 28.1, 22.7, 22.5. GC–MS *m/e* 147 (49%), 146 (30%), 131 (100%), 118 (81%), 117 (38%), 105 (77%), 104 (35%), 103 (15%), 91 (68%), 79 (32%), 78 (19%), 77 (38%), 67 (17%), 65 (25%), 53 (15%), 51 (25%), 49 (32%), 41 (33%), 39 (33%).

4.2.20. 1,2,3,4,5,6,7,8-Octahydro-2,3-bis(methylene)-naphthalene (28) [Table 1, entry 5]. 2-[(Chloromethyl)-sulfonyl]-3-methylene-1,2,3,4,5,6,7,8-octahydronaphthalene (1.9 g, 7.29 mmol) in THF (10 mL) was cooled to 0 °C under argon. A solution of KO*t*Bu in THF (1 M, 16 mL, 16 mmol) was added dropwise. The mixture was stirred for 30 min and was quenched with saturated aqueous NH_4Cl. Diethyl ether was added and the organic layer was dried. The solvents were removed in vacuo and the residue was passed through a short column (5 cm; pentane) and the solution was concentrated again giving known **28**[21] as a colorless oil (1.0 g, 86%); ^{1}H NMR δ 5.08 (d, *J*=2 Hz, 2H), 4.75 (d, *J*=2 Hz, 2H), 2.81 (s, 4H), 1.91 (br s, 4H), 1.62 (quin., *J*=3.3 Hz, 4H); ^{13}C NMR δ 146.0, 126.7 (both C), 108.1, 38.6, 29.7, 23.0 (all CH_2); GC–MS *m/z* 160 (M^+, 64%), 145 (29%), 131 (32%), 117 (76%), 115 (36%), 92 (55%), 91 (100%), 77 (36%), 41 (37%), 39 (57%).

4.2.21. 1,2,3,4,5,6,7,8,9,10-Decahydro-2,3-bis(methylene)-anthracene (29) [Table 1, entry 6]. A 25 mL flask was charged with **28** (1.0 g, 6.25 mmol) and **4** (0.8 g, 5.26 mmol). The mixture was heated for 3 h at 60 °C, diluted with THF (5 mL), cooled to 0 °C and KO*t*-Bu (0.59 g, 5.26 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 15 min, quenched with saturated aqueous NH_4Cl, diluted with diethyl ether, and the organic layer was removed, dried, concentrated in vacuo, and chromatographed (pentane) giving **29** (0.95 g; 85%) as a waxy solid: ^{1}H NMR δ 5.09 (d, *J*=2 Hz, 2H), 4.75 (d, *J*=2 Hz, 2H), 2.80 (m, 8H), 1.92 (br s, 4H), 1.62 (m, 4H); ^{13}C NMR δ 145.7, 125.5, 124.5 (all C), 108.3, 37.5, 36.7, 29.5, 23.2 (all CH_2); GC–MS *m/z* 212 (M^+, 80%), 197 (54%), 169 (60%), 155 (100%), 141 (52%), 129 (35%), 128 (37%), 115 (39%), 91 (40%), 77 (34%); EI HRMS calcd for $C_{16}H_{20}$: 212.1565. Found 212.1559.

4.2.22. 1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-2,3-bis-(methylene)naphthacene (30) [Table 1, entry 7]. Compounds **29** (0.5 g, 2.36 mmol) and **4** (0.36 g, 2.36 mmol) was kept in a screw capped vial maintained at 60 °C for 3 h. The product was then transferred to a 25 mL three-necked flask, dissolved in THF (10 mL), cooled to 0 °C and KO*t*-Bu

(0.26 g, 2.36 mmol) in THF (3 mL) was added dropwise. The solution was stirred for 15 min, quenched with saturated aqueous NH_4Cl, and the organic layer was separated, dried, concentrated in vacuo, and chromatographed (pentane) giving **30** (0.49 g, 85%) as a waxy solid: ^{1}H NMR δ 5.09 (d, J=2 Hz, 2H), 4.77 (d, J=2 Hz, 2H), 2.77 (m, 12H), 1.93 (br s, 4H), 1.61 (m, 4H); ^{13}C NMR, δ 146.1, 126.7, 125.6, 124.9 (all C), 108.3, 39.2, 38.5, 36.7, 29.7, 22.9 (all CH_2); GC–MS m/z 264 (M^+, 83%), 231 (57%), 203 (65%), 189 (100%); EI HRMS calcd for $C_{20}H_{24}$: 264.1878. Found: 264.1881.

4.2.23. 1,2-Dimethyl-4,5-bis(methylene)cyclohexene (31) [Table 1, entry 8]. A 2 mL screw capped vial was charged with **4** (0.1 g, 0.66 mmol), 2,3-dimethyl-1,3-butadiene (0.2 g, 2.4 mmol), sealed and maintained at 80 °C. The reaction was complete in 5 h, as verified by GC (GC–MS m/z 121 (26%), 120 (26%), 105 (100%), 93 (15%), 91 (32%), 79 (20%), 77 (25%), 65 (10%), 51 (13%), 49 (14%), 41 (16%), 39 (20%)). The product was placed in a 50 mL flask, dissolved in THF (10 mL) under N_2, cooled to 0 °C and a solution of KOt-Bu (0.114 g, 0.66 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 15 min, quenched with saturated aqueous NH_4Cl, diluted with diethyl ether (10 mL), and the organic layer was separated, dried, and concentrated in vacuo. Chromatography (pentane) gave **31** (0.05 g, 57%) as a colorless oil: ^{1}H NMR δ 5.08 (d, J=2.2 Hz, 2H), 4.74 (d, J=2.2 Hz, 2H), 2.85 (br s, 4H), 1.65 (br s, 6H); ^{13}C NMR δ 146.0 (C), 124.4 (C), 107.9 (CH_2), 39.7 (CH_2), 18.6 (CH_3); GC–MS m/z 134 (M^+, 38%), 119 (49%), 117 (17%), 105 (23%), 92 (18%), 91 (100%), 79 (20%), 77 (25%), 65 (17%), 51 (21%), 41 (37%), 39 (52%); EI HRMS calcd for $C_{10}H_{14}$: 134.1095. Found 134.1094.

4.2.24. (*E*,*Z*)-5-Methylene-6-(undecylidene)bicyclo-[2.2.1]hept-2-ene (32) [Table 1, entry 9]. A screw capped vial was charged with **14** (0.1 g, 0.3 mmol), and freshly distilled cyclopentadiene (0.07 g, 1.0 mmol). The tube was sealed and maintained at 100 °C for 30 min. The reaction was followed by TLC (CH_2Cl_2/hexane (5:1)). The product was dissolved in THF (5 mL), placed in a 50 mL three-necked flask under N_2, and cooled to 5 °C. A THF (5 mL) solution of KOt-Bu (0.033 g, 0.3 mmol) was added dropwise turning the solution a pale yellow color. The solution was stirred for 15 min, quenched with saturated aqueous NH_4Cl, treated with diethyl ether (10 mL), and the organic layer was separated, dried, concentrated in vacuo and chromatographed (hexane) giving **32** (0.048 g, 60%) as a colorless oil: ^{1}H NMR δ 6.26 (br s, 2H), 5.55 (t, J=4 Hz, 1H), 5.15 (d, J=4 Hz, 2H), 3.27 (br s, 1H), 3.18 (br s, 1H), 2.23 (m, 2H), 1.68 (dd, J=8, 4 Hz, 2H), 1.41 (m, 2H), 1.29 (s, 16H), 0.88 (t, J=4 Hz, 3H); ^{13}C NMR δ 150.3 (C), 137.5 (CH), 136.5 (CH), 125.4 (C), 124.6 (CH), 106.4 (CH_2), 53.6, 52.7 (both CH), 31.9, 29.8, 29.7, 29.5, 29.5, 29.4, 29.2, 29.0, 28.9, 28.7, 22.7 (all CH_2), 14.1 (CH_3); GC–MS m/z 272 (M^+, 0.2%), 131 (59%), 117 (57%), 91 (68%), 66 (61%), 43 (75%), 41 (100%); EI HRMS calcd for $C_{20}H_{32}$: 272.2504. Found 272.2501.

4.2.25. (*E*,*Z*)-5-Methylene-6-undecylidene-7-oxabicyclo-[2.2.1]hept-2-ene (33) [Table 1, entry 10]. A screw capped vial was charged with **14** (0.1 g, 0.33 mmol) and furan (0.068 g, 1.0 mmol). The vial was sealed and kept at 120 °C for 2 h. The product was dissolved in THF (5 mL) and placed in a 50 mL three-necked flask under N_2 at 5 °C. A THF (5 mL) solution of KOt-Bu (0.37 g, 0.33 mmol) was added dropwise giving a deep red color. Diethyl ether (10 mL) was added and the organic layer was separated, dried and concentrated in vacuo. Chromatography of the deep red oil (CH_2Cl_2/hexane (5:1)) gave **33** (0.45 g, 49%) as a colorless waxy solid: ^{1}H NMR δ 6.5 (d, J=2 Hz, 2H), 5.65 (t, J=4 Hz, 1H), 5.3 (m, 2H), 5.1 (m, 2H), 2.3 (m, 2H), 1.45 (m, 2H), 1.3 (s, 16H), 0.88 (t, J=4 Hz, 3H); ^{13}C NMR δ 143.2 (C), 142.1 (C), 136.4, 135.4, 125.7 (all CH), 107.2 (CH_2), 84.8 (CH), 84.5, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.4, 22.7 (all CH_2), 14.1 (CH_3); GC–MS m/z 274 (M^+, 0.6%), 133 (35%), 120 (33%), 105 (44%), 91 (100%), 55 (34%), 43 (66%), 41 (92%); EI HRMS calcd for $C_{17}H_{30}O$: 274.2297. Found 274.2293.

4.2.26. 5-Isopropylidene-6-(methylene)bicyclo[2.2.1]-hept-2-ene (34) [Table 1, entry 11]. A screw capped vial was charged with **13** (0.5 g, 2.78 mmol) and freshly distilled cyclopentadiene (0.25 g, 3.79 mmol). By GC, the reaction was complete after 1 h at room temperature. (GC–MS m/z 248 (M^+, ^{37}Cl, 0.65%), 246 (M^+, ^{35}Cl, 1.5%), 133 (80%), 105 (58%), 91 (100%), 77 (21%), 67 (23%), 66 (40%), 65 (27%), 55 (23%), 51 (21%), 49 (18%), 41 (43%), 39 (41%)). The product was dissolved in THF (25 mL) and transferred to a 50 mL three-necked round bottom flask. The solution was cooled to 0 °C and a THF (5 mL) solution of KOt-Bu (0.31 g, 2.78 mmol) was added dropwise, turning the solution a deep red-black color. The solution was then quenched with saturated aqueous NH_4Cl, the organic layer was separated, dried, concentrated in vacuo and the residue chromatographed (pentane) giving the **34** slightly contaminated with dicyclopentadiene (0.31 g, 85%) by GC: ^{13}C NMR δ 147.1 (C), 147.2 (C), 137.3 (CH), 137.4 (CH), 131.3 (C), 105.4 (CH_2), 65.3 (CH_2), 54.2 (CH), 52.1 (CH), 30.2 (CH_3); GC–MS m/z 146 (M^+, 54%), 131 (100%), 91 (74%), 80 (77%), 79 (85%), 77 (45%), 66 (42%), 65 (40%), 51 (38%), 41 (31%), 39 (83%); EI HRMS calcd for $C_{11}H_{14}$: 146.1096. Found 146.1099.

4.2.27. 4-[(Chloromethyl)sulfonyl]-1,2-dimethylcyclohexene (35) [Table 1, entry 12]. A mixture of 2,3-dimethylbutadiene (3.2 mL, 28.6 mmol) and **5** (2.05 g, 14.6 mmol) in toluene (4 mL) was heated in a sealed tube at 120–130 °C for 12 h. The product was concentrated in vacuo and chromatographed (5:1 hexane/EtOAc) yielding the title compound (3.12 g, 96%) as a colorless solid, mp 69–70 °C; IR (film) 1309 (SO_2), 1146 (SO_2) cm^{-1}; ^{1}H NMR δ 4.43 (s, 2H), 3.47 (m, 1H), 2.41–2.07 (m, 5H), 1.71 (m, 1H), 1.60 (s, 3H), 1.57 (s, 3H); ^{13}C NMR δ 125.8, 122.0, 55.1, 53.6, 30.3, 29.5, 21.2, 18.8, 18.7. Anal. Calcd for $C_9H_{15}ClO_2S$: C, 48.53; H, 6.79 Found: C, 48.50; 7.44.

4.2.28. 1,2-Dimethyl-4-(methylene)cyclohexene (36) [Table 1, entry 12]. A solution of KOt-Bu (12.0 mL, 12.0 mmol, 1 M) in THF was added to 4-chloromethanesulfonyl-1,2-dimethylcyclohexene (1.34 g, 6.0 mmol) in THF (15 mL) at 0 °C. The mixture was heated at reflux for 1 h and then treated with CH_2Cl_2 (150 mL) and water (30 mL). The organic layer was washed with water (10×30 mL), dried, filtered through a silica gel pad, and

the solvent (CH_2Cl_2) was removed by distillation yielding known **36**[17a] as a colorless oil (429 mg, 59%); ^{1}H NMR δ 4.68 (s, 2H), 2.67 (s, 2H), 2.26 (t, J=6.5 Hz, 2H), 2.07 (m, 2H), 1.61 (s, 6H); ^{13}C NMR δ 147.0, 125.8, 124.9, 106.4, 39.7, 39.7, 33.9, 32.3, 18.8; GC–MS *m/z* (rel. intensity) 122 (M^+, 85), 107 (100), 91 (92), 79 (93).

4.2.29. 5-[(Chloromethyl)sulfonyl]bicyclo[2.2.2]oct-2-ene (37) [Table 1, entry 13]. A mixture of 1,3-cyclohexadiene (2.72 mL, 28.6 mmol) and **5** (2.09 g, 14.9 mmol) in toluene (1 mL) was heated in a sealed tube at 120–130 °C for 12 h. The product was concentrated in vacuo and chromatographed (5:1 hexane/EtOAc) yielding **37** (3.1 g, 95%) as a colorless oil which by NMR was a 6.3:1 *endo*/*exo* mixture; *exo*: R_f 0.45 hexanes/EtOAc 5:1; IR (neat) 1319 (SO_2), 1146 (SO_2), 1120 (SO_2) cm^{-1}; ^{1}H NMR δ 6.39 (m, 2H), 4.45 and 4.35 (AB_q, J=12.6 Hz, 2H), 3.30 (m, 1H), 3.18 (br s, 1H), 2.75 (br s, 1H), 1.20–2.24 (m, 6H); ^{13}C NMR δ 136.1, 133.5, 56.5, 55.4, 29.3, 29.2, 27.3, 24.5, 20.4; *endo*: R_f 0.36 hexanes/EtOAc 5:1; IR (neat) 1319 (SO_2), 1147 (SO_2), 1122 (SO_2); ^{1}H NMR δ 6.41 (m, 1H), 6.28 (m, 1H), 4.35 (s, 2H), 3.60 (m, 1H), 3.17 (br s, 1H), 2.78 (br s, 1H), 1.24–2.04 (m, 6H); ^{13}C NMR δ 135.1, 130.4, 58.3, 54.3, 29.2, 29.0, 28.8, 26.1, 22.9.

4.2.30. 5-Methylenebicyclo[2.2.2]oct-2-ene (38) [Table 1, entry 13]. A solution of KO*t*-Bu in THF (12 mL, 12 mmol, 1 M) was added to **37** (1.32 g, 6.0 mmol) in THF (15 mL) at 0 °C. The mixture was heated at reflux for 1 h and then mixed with CH_2Cl_2 (150 mL) and water (30 mL). The organic layer was washed with water (10×30 mL), dried, and filtered through a silica gel pad. The solvent was removed by distillation yielding known **38**[17c] as a colorless oil (366 mg, 51%): ^{1}H NMR δ 6.26 (m, 2H), 4.74 (m, 1H), 4.55 (m, 1H), 3.00 (m, 1H), 2.65 (m, 1H), 2.25–2.18 (m, 2H), 1.66–1.54 (m, 4H); ^{13}C NMR δ 150.7, 134.1, 133.0, 103.8, 41.0, 34.9, 31.4, 29.7, 26.5; GC–MS *m/z* (rel. intensity) 120 (M^+, 35), 92 (100), 91 (92), 79 (38), 77 (37).

4.2.31. 11-[(Chloromethyl)sulfonyl]-9,10-dihydro-9,10-ethanoanthracene (39) [Table 1, entry 14]. A mixture of anthracene (1.35 g, 7.14 mmol) and **5** (0.5 g, 3.57 mmol) in toluene (1.5 mL) was heated in a sealed tube at 155 °C for 7 h. The reaction mixture was taken up in $CHCl_3$ (30 mL), anthracene (0.15 g) was removed by filtration, the filtrate was concentrated in vacuo and the residue chromatographed (1:1 pentane/$CHCl_3$, then $CHCl_3$) gave **39** as a colorless solid (1.12 g, 96%), mp 143–145 °C; IR (film) 1322 (SO_2), 1146 (SO_2), 1118 (SO_2) cm^{-1}; ^{1}H NMR δ 7.46–7.16 (m, 8H), 5.00 (d, J=2.1 Hz, 1H), 4.86 (*t*, J=2.7 Hz, 1H), 4.16 (AB_q, J=12.7, 2H), 3.74 (ddd, J=2.4, 6.3, 9.3 Hz, 1H), 2.30–2.26 (m, 2H); ^{13}C NMR δ 143.3, 143.2, 140.9, 137.9, 127.1, 127.0, 126.6, 126.5, 125.6, 124.0, 124.0, 123.6, 59.5, 55.6, 43.5, 43.3, 30.2.

4.2.32. 9,10-Dihydro-11-methylene-9,10-ethanoanthracene (40) [Table 1, entry 14]. A solution of KO*t*-Bu in THF (4.08 mL, 4.08 mmol, 1 M) was added to **39** (0.67 g, 2.04 mmol) in THF (10 mL) at 0 °C. The reaction mixture was heated at reflux for 1 h, concentrated in vacuo, and the residue was treated with ether (20 mL) and water (20 mL). The aqueous layer was extracted with ether (2×20 mL), organic phase washed with water (2×20 mL), dried, and concentrated in vacuo, affording known **40**[17a] as colorless crystals (0.39 g, 89%), mp 104–105 °C (lit. mp 101–102 °C[17a]); ^{1}H NMR δ 7.51–7.29 (m, 8H), 5.35 (br s, 1H), 4.94 (d, J=10.2 Hz, 2H), 4.55 (m, 1H), 2.65 (m, 2H); ^{13}C NMR δ 146.5, 143.4, 142.5, 126.2, 123.7, 123.6, 107.4, 107.4, 55.5, 45.0, 35.4; GC *m/z* (rel. intensity) 218 (M^+, 28), 178 (100).

4.2.33. 2-[(Chloromethyl)sulfonyl]-1,2,3,4,5,6,7,8-octahydronaphthalene (41) [Table 1, entry 15]. A mixture of 1,2-bis(methylene)cyclohexane (1.3 g, 12 mmol) and **5** (1.55 g, 11 mmol) in toluene (3 mL) was heated at 110–120 °C in a sealed tube for 16 h, the mixture concentrated in vacuo and chromatographed (5:1 hexane/EtOAc) to afford **41** (2.41 g, 97%) as colorless crystals, mp 81–82 °C; ^{1}H NMR δ 4.44 (s, 2H); 3.49–3.61 (m, 1H), 1.65–2.42 (m, 12H), 1.41–1.54 (m, 2H); ^{13}C NMR δ 128.4, 124.6, 55.1, 53.3, 30.1, 29.8, 29.2, 28.6, 22.8, 21.2; IR (neat), 725 (C–Cl), 1156 (s), 1332 cm^{-1} (s, SO_2). Anal. Calcd for $C_{11}H_{17}ClO_2S$ C, 53.11; H, 6.89. Found, C, 52.78; H, 6.50 (see Scheme 18).

4.2.34. 1,2,3,4,5,6,7,8-Octahydro-2-methylenenaphthalene (42) [Table 1, entry 15]. A solution of KO*t*Bu in THF (1 M, 10.0 mL, 10.0 mmol) was added dropwise at 0 °C to **41** (1.24 g, 5.0 mmol) in THF (20 mL). The reaction mixture was refluxed for 1 h., concentrated in vacuo, and the residue was treated with ether (40 mL) and water (40 mL). The layers were separated and the aqueous layer was extracted with ether (3×40 mL). The combined ether layers were washed with water (2×30 mL), dried, concentrated in vacuo and chromatographed (pentane) to give **42** (584 mg, 79%) as a colorless oil; ^{1}H NMR δ 4.67 (s, 2H); 2.60 (s, 2H), 2.26 (t, J=6.6 Hz, 2H), 2.00 (t, J=6.1 Hz, 2H), 1.85 (br, 4H), 1.54–1.64 (m, 4H); ^{13}C NMR δ 147.0, 128.1, 127.3, 106.6, 38.6, 32.8, 32.1, 30.1, 30.0, 23.1, 23.0; EI MS: *m/z* 148 (M^+, 100), 133 (38), 119 (27), 105 (48), 91 (28); IR (neat) 2919 cm^{-1} (C=CH), 1649 (C=C), 1443 (C=CH), 885 cm^{-1} (C=CH).

4.2.35. 2-[(Chloromethyl)sulfonyl]-1,2,3,4,5,6,7,8,9,10-decahydroanthracene (43) [Table 1, entry 16]. Compound **5** (141 mg, 1.0 mmol) and **28** (320 mg, 2 mmol) were sealed in a tube and the mixture was heated to 60 °C and stirred for 12 h. The mixture was concentrated in vacuo and chromatographed (6:1 hexane/EtOAc) to yield the title compound (277 mg, 92%) as a colorless powder, mp 123–124 °C; ^{1}H NMR δ 4.45 (s, 2H); 3.54–3.64 (m, 1H), 2.31–2.60 (m, 5H), 2.10–2.30 (m, 4H), 1.80–1.90 (m, 5H), 1.60–1.65 (m, 4H); ^{13}C NMR δ 126.2, 125.5, 125.3, 122.5, 73.1, 55.0, 53.3, 36.8, 29.3, 28.3, 27.8, 23.9, 23.0, 21.1; IR ($CHCl_3$): 1161, 1322 cm^{-1} (SO_2). Anal. Calcd for $C_{15}H_{21}ClO_2S$: C, 59.88; H, 7.04. Found: C, 60.16; H, 6.65.

4.2.36. 1,2,3,4,5,6,7,8,9,10-Decahydro-2-methyleneanthracene (44) [Table 1, entry 16]. A solution of 2-[(chloromethyl)sulfonyl]-1,2,3,4,5,6,7,8,9,10-decahydroanthracene (301 mg, 1 mmol) in THF (5 mL) was cooled to −5 °C under Ar. A solution of KO*t*Bu in THF (1 M, 2.0 mL, 2.0 mmol) was added dropwise. The mixture was stirred for 30 min and was quenched with saturated aqueous NH_4Cl. Diethyl ether was added and the organic layer was dried.

The solvents were removed in vacuo, the residue was filtered through a short silica gel column (5 cm; pentane) and the solution was concentrated again. Compound **44** was obtained as a colorless oil (150 mg; 75%); ^{1}H NMR δ 4.70 (s, 2H), 2.64 (s, 2H), 2.41 (s, 4H), 2.31 (t, J=6.5 Hz, 2H), 2.03 (t, J=6.5 Hz, 2H), 1.86 (br, 4H), 1.54–1.64 (m, 4H); ^{13}C NMR δ 146.6, 126.0, 125.7, 125.6, 125.2, 107.0, 37.6, 37.2, 37.1, 32.1, 31.8, 29.4, 23.2; EIMS: m/z 200 (M^+, 100), 157 (18), 145 (63), 129 (15), 117 (13); IR (neat) 2926 (C═CH), 1653 (C═C), 1436 (C═CH), 881 (C═CH) (see Scheme 17).

4.2.37. 4-[(Chloromethyl)sulfonyl]-1-(4-methyl-1-pent-3-enyl)cyclohexene and 5-[(chloromethyl)sulfonyl]-1-(4-methyl-1-pent-3-enyl)cyclohexene (45a,b) [Table 1, entry 17]. A mixture of myrcene (0.97 g, 7.14 mmol) and **5** (0.5 g, 3.57 mmol) in toluene (1.5 mL) was heated in a sealed tube at 145 °C for 7 h; the mixture was concentrated in vacuo and chromatographed (5:1 hexane/EtOAc) yielding a 2.3:1 **45a/45b** mixture (0.75 g, 76%; an oil); IR (neat) 1320 (SO_2), 1146 (SO_2), 1119 (SO_2) cm^{-1}; ^{1}H NMR **45a**, δ 5.37 (m, 1H), 5.04 (m, 1H), 4.44 (s, 2H), 3.60–3.44 (m 1H), 2.38–1.95 (m, 10H), 1.65 (s, 3H), 1.56 (s, 3H); **45b** had additional peaks at δ 5.47 (m, 1H), 4.67 (d, J=15 Hz, 1H), 4.45 (s, 2H), 1.69 (s, 3H), 1.54 (s, 3H), integrated relative to the minor component (**45b**) peaks; ^{13}C NMR (**45a**) 138.0, 131.9, 123.6, 116.7, 55.0, 53.4, 37.3, 27.4, 26.8, 25.8, 24.0, 20.9, 17.7. Anal. Calcd for $C_{13}H_{21}ClO_2S$: C, 56.40; H, 7.65. Found: C, 56.48; 8.34.

4.2.38. 4-Methylene-1-(4′-methylpent-3-enyl)-cyclohexene and 5-methylene-1-(4′-methylpent-3-enyl)-cyclohexene (46a,b) [Table 1, entry 17]. A solution of potassium *tert*-butoxide (1 M in THF, 6.3 mL, 6.3 mmol) was added dropwise to a solution of **45a**,**b** (830 mg, 3.0 mmol) in THF (15 mL). The mixture was refluxed for 1 h, quenched with NH_4Cl solution, concentrated in vacuo, and the residue taken up in ether (30 mL) and water (30 mL). The layers were separated and the aqueous layer was extracted with ether (3×40 mL). The combined ether layers were washed with water (3×20 mL) and dried ($MgSO_4$), concentrated in vacuo and the residue chromatographed (pentane) yielding 2.54:1 **46a/46b** (476 mg, 90%) as a colorless oil; **46a**: ^{1}H NMR δ 5.34 (br, 1H), 5.09 (t, J=6.9 Hz, 1H), 4.71 (s, 2H), 2.75 (br, 2H), 2.31–1.92 (m, 8H), 1.67 (s, 3H), 1.58 (s, 3H); ^{13}C NMR δ 146.3, 137.8, 131.4, 124.3, 119.8, 107.2, 37.6, 33.5, 31.9, 30.8, 26.5, 25.7, 17.7; **46b**: ^{1}H NMR δ 5.43 (br, 1H), 5.09 (t, J=6.9 Hz, 1H), 4.71 (s, 2H), 2.68 (br, 2H), 2.31–1.92 (m, 8H), 1.67 (s, 3H), 1.58 (s, 3H); ^{13}C NMR δ 146.5, 137.1, 131.5, 124.3, 120.6, 107.1, 37.4, 36.9, 31.9, 31.6, 27.4, 26.4, 17.7; EI GC–MS m/z 176 (M^+, 9%), 107 (26%), 91 (64%), 79 (45%), 69 (100%). The structure of the compound was established by heating a portion of **46a**,**b** (190 mg, 1.08 mmol) with sulfur (34.5 mg, 1.08 mmol) at 200 °C for 12 h. Chromatography (hexanes) of the product gave as the major product 4-methyl-1-(4′-methylpent-3′-enyl)benzene (**46c**; 50 mg, 26%) which could be identified by the simplicity of its ^{1}H and ^{13}C NMR spectra, compared to the spectra expected for the *meta* isomer; ^{1}H NMR δ 7.08 (s, 4H), 5.19 (m, 1H), 2.55–2.62 (m, 2H), 2.31 (s, 3H), 2.35–2.05 (m, 2H), 1.69 (s, 3H), 1.58 (s, 3H); ^{13}C NMR δ 139.4, 135.1, 132.1, 129.0, 128.2, 123.9, 35.8, 30.2, 25.8, 21.1, 17.8.

4.2.39. 1-*tert*-Butyl-4-[(chloromethyl)sulfonyl]cyclohexene and 1-*tert*-butyl-5-[(chloromethyl)sulonyl]cyclohexene (47a,b) [Table 1, entry 18]. 2-*tert*-Butylbuta-1,3-diene (825 mg, 7.5 mmol) and **5** (703 mg, 5 mmol) were placed in a sealed tube and heated to 130–150 °C with stirring for 12 h. Volatiles were removed in vacuo and the residue was chromatographed (hexane/ethyl acetate, 6:1) to yield 2.6:1 **47a/47b** (962 mg, 74%) as a colorless oil; **47a**: ^{1}H NMR δ 5.40 (m, 1H), 4.44 (s, 2H), 3.38–3.48 (m, 1H), 1.60–2.40 (m, 6H), 1.00 (s, 9H); **47b** had additional peaks at δ 5.42–5.45 (m, 1H), 4.47 (d, J=3.21 Hz, 1H), 1.03 (s, 9H). Anal. Calcd for $C_{11}H_{19}ClO_2S$: C, 52.68; H, 7.64. Found: C, 52.10; H, 7.13.

4.2.40. 1-*t*-Butyl-4-(methylene)cyclohexene and 1-*t*-butyl-5-(methylene)cyclohexene (48a, 48b) [Table 1, entry 18]. A THF solution of KO*t*-Bu (1 M in THF, 4.4 mL, 4.4 mmol) was added dropwise to **47a**,**b** (501 mg, 2.0 mmol) in THF (10 mL). The mixture was refluxed for 1 h, quenched with NH_4Cl solution, concentrated in vacuo, and the residue mixed with ether (20 mL) and water (20 mL). The layers were separated and the aqueous layer was extracted with ether (3×40 mL). The combined ether layers were washed with water (3×15 mL), dried ($MgSO_4$), concentrated in vacuo, and the residue chromatographed (pentane) yielding a 2.5:1 **48a/48b** mixture (200 mg, 67%) as a colorless oil; **48a**: ^{1}H NMR δ 5.29 (t, J=3.6 Hz, 1H), 4.60 (s, 2H), 2.65–2.68 (m, 2H), 2.05–2.19 (m, 4H), 0.90 (s, 9H); ^{13}C NMR δ 146.6, 145.8, 116.6, 106.7, 35.3, 33.6, 31.6, 28.9, 27.0; **48b**: ^{1}H NMR δ 5.40 (m, 1H), 4.62 (s, 2H), 2.65–2.68 (m, 2H), 2.05–2.19 (m, 4H), 0.92 (s, 9H); ^{13}C NMR δ 147.2, 145.0, 128.3, 117.4, 34.7, 33.1, 31.6, 29.1, 27.5.

4.2.41. Trichloro(methylsulfonyl)methane (49). Dimethyl sulfone (1.5 g, 15.9 mmol) and SO_2Cl_2 (150 mL) were placed in a photoreactor fitted with a Hanovia 450 W UV lamp, wrapped with nichrome heating wire, and containing at the bottom a gas bubbling tube and topped by a condenser. The mixture was electrically heated to a gentle reflux as Cl_2 was slowly introduced. The refluxing solution was irradiated for 2.5 h while monitoring TLC. The mixture was then concentrated in vacuo, collecting the SO_2Cl_2 for further use. The residue was chromatographed (5:1 hexane/EtOAc) giving known **49**[18a] as colorless crystals (2.86 g, 91%), mp 163–165 °C; ^{1}H NMR δ 3.35 (s, 3H); ^{13}C NMR δ 103.1, 33.4.

4.2.42. 4-[(Dichloromethyl)sulfonyl]-1,2-dimethylcyclohexene (50) [Table 1, entry 19]. A solution of **6** (1.0 g, 5.7 mmol) and 2,3-dimethylbuta-1,3-diene (1.0 g, 11.4 mmol) in toluene (2 mL) was heated to 100 °C in a sealed tube overnight, the mixture concentrated in vacuo and chromatographed (5:1 hexane/ethyl acetate) giving **50** (1.36 g, 93%) as colorless crystals, mp 71–72 °C; ^{1}H NMR δ 6.28 (s, 1H), 3.70–3.82 (m, 1H), 2.47 (t, J=13.2 Hz, 1H), 2.20–2.32 (m, 2H), 2.10–2.20 (m, 2H), 1.80–1.90 (m, 1H), 1.64 (s, 3H), 1.61 (s, 3H); ^{13}C NMR δ 126.0, 122.0, 55.6, 30.2, 19.0, 18.7; IR (neat): 777 (CCl_2), 1140, 1332 (SO_2), 1643, 1659 cm^{-1} (C═C). Anal. Calcd for $C_9H_{14}Cl_2O_2S$: C, 42.03; H, 5.49. Found C, 42.21; H, 5.16.

4.2.43. 4-(Dichloromethylene)-1,2-dimethylcyclohexene (51) [Table 1, entry 19]. A solution of **50** (300 mg,

1.17 mmol) and $MeSO_2CCl_3$ (300 mg, 1.62 mmol) in THF (12 mL) was cooled to −3 °C under Ar. A solution of KO*t*Bu in THF (1 M, 2.34 mL, 2.34 mmol) was added dropwise. The reaction mixture was stirred for 1 h at 0 °C and was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with ether (2×20 mL). The combined ether layers were dried, concentrated in vacuo and chromatographed (hexane) to give the title compound (160 mg, 72%) as a colorless oil; ^{1}H NMR δ 2.85 (s, 2H), 2.50 (t, J=6.5 Hz, 2H), 2.09 (t, J=5.5 Hz, 2H), 1.66 (s, 6H); ^{13}C NMR δ 135.7, 126.1, 123.3, 111.5, 36.7, 31.6, 29.7, 28.7, 18.7; EI MS *m*/*z* 192 (M^++2, 63), 190 (M^+, 99), 177 (50), 175 (81), 155 (76), 139 (66), 119 (96), 91 (100), 77 (83), 51 (63); IR (neat): 1622 cm^{-1} (C═C).

4.2.44. 5-[(Dichloromethyl)sulfonyl]bicyclo[2.2.2]oct-2-ene (52) [Table 1, entry 20]. A mixture of cyclohexa-1,3-diene (800 mg mL, 10 mmol) and **6** (2.6 g, 15 mmol) in toluene (5 mL) was heated in a sealed tube at 120–130 °C for 12 h. The product was concentrated in vacuo and chromatographed (5:1 hexane/EtOAc) yielding **52** (2.34 g, 92%) as colorless crystals, mp 121–122 °C which by NMR was found to be a 3:1 *endo*/*exo* mixture; ^{1}H NMR δ 6.41 (t, J=6.8 Hz, 1H), 6.27 (t, J=6.8 Hz, 1H), 6.10 (s, 1H), 3.80–3.85 (m, 1H), 3.20–3.3 (m, 1H), 2.70–2.80 (m, 1H), 1.90–2.20 (m, 2H), 1.55–1.67 (m, 2H), 1.31–1.43 (m, 2H); ^{13}C NMR δ 135.4, 130.1, 78.2, 57.9, 30.0, 29.9, 29.3, 25.7, 23.0; IR (CH_2Cl_2) 1147, 1336 cm^{-1} (SO_2). Anal. Calcd for $C_9H_{12}Cl_2O_2S$: C, 42.36; H, 4.74. Found: C, 42.41; H, 5.10.

4.2.45. 5-(Dichloromethylene)bicyclo[2.2.2]oct-2-ene (53) [Table 1, entry 20]. Compound **52** (255 mg, 1.0 mmol) and **49** (296 mg, 1.5 mmol) in THF (12 mL) were cooled to −3 °C under Ar and KO*t*-Bu (1 M in THF, 2.0 mL, 2.0 mmol) was added dropwise. The reaction mixture was stirred for 1 h at 0 °C, quenched with saturated aqueous NH_4Cl solution, extracted with ether (2×20 mL), the combined ether layers dried, concentrated in vacuo and the residue chromatographed (hexane) to yield **53** (136 mg, 72%) as a colorless oil; ^{1}H NMR δ 6.39 (t, J=6.7 Hz, 1H), 6.26 (t, J=6.7 Hz, 1H), 3.63–3.65 (m, 1H), 2.80–2.82 (m, 1H), 2.06–2.22 (m, 2H), 1.50–1.67 (m, 2H), 1.34–1.46 (m, 2H); ^{13}C NMR δ 140.0, 135.8, 131.1, 36.9, 31.2, 29.7, 24.6, 24.2; EI MS: *m*/*z* 190 (M^++2, 10), 188 (M^+, 16), 160 (54), 125 (100); IR (neat): 3048, 1626, 1444, 899 (C═C), 1463, 709 cm^{-1} (CCl_2).

4.2.46. 2-[(Dichloromethyl)sulfonyl]-1,2,3,4,5,6,7,8-octahydronaphthalene (54) [Table 1, entry 21]. A solution of **6** (1.0 g, 5.7 mmol) and 1,2-bis(methylene)cyclohexane (1.23 g, 11.4 mmol) in toluene (2 mL) was heated to 100 °C in a sealed tube overnight. The mixture was concentrated in vacuo and chromatographed (5:1 hexane/EtOAc) yielding **54** (1.52 g, 94%) as colorless crystals, mp 91–93 °C; ^{1}H NMR δ 6.27 (s, 1H), 3.75–3.85 (m, 1H), 2.42 (t, J=12.6 Hz, 1H), 2.15–2.30 (m, 2H), 2.03–2.11 (m, 2H), 1.80–1.90 (m, 5H), 1.62–1.75 (m, 2H), 1.40–1.52 (m, 2H); ^{13}C NMR δ 128.4, 124.5, 55.5, 30.0, 29.8, 29.1, 22.8, 21.8; IR ($CHCl_3$) 1140, 1322 cm^{-1} (SO_2). Anal. Calcd for $C_{11}H_{16}Cl_2O_2S$: C, 46.65; H, 5.69. Found: C, 46.81; H, 5.32.

4.2.47. 2-(Dichloromethylene)-1,2,3,4,5,6,7,8-octahydronaphthalene (55) [Table 1, entry 21]. A solution of **54** (566 mg, 2.0 mmol) and **49** (742 mg, 4.0 mmol) in THF (15 mL) was cooled to 0 °C under Ar. A solution of KO*t*Bu in THF (1 M, 4.0 mL, 4.0 mmol) was added dropwise. The reaction mixture was stirred for 1 h at 0 °C and was quenched with saturated aqueous NH_4Cl. The mixture was extracted with ether (2×20 mL), dried, concentrated in vacuo and chromatographed (hexane) yielding **55** (150 mg, 65%) as a colorless oil; ^{1}H NMR δ 2.79 (s, 2H), 2.51 (t, J=6.5 Hz, 2H), 2.02 (t, J=6.5 Hz, 2H), 1.83–1.88 (m, 4H), 1.59–1.63 (m, 4H); ^{13}C NMR δ 135.5, 128.4, 125.7, 111.6, 35.7, 30.4, 29.9, 29.8, 29.7, 28.5, 22.9; EI MS: *m*/*z* 218 (M^++2, 62), 216 (M^+, 93), 181 (100), 145 (80), 117 (30), 91 (55); IR (neat): 715 (CCl_2), 1643, 1664 cm^{-1} (C═C).

4.2.48. Chloromethylene-1,2,3,4,5,6,7,8-octahydronaphthalene (56) [Table 1, entry 22]. To a solution of **54** (283 mg, 1.0 mmol) in 60 mL of THF KO*t*-Bu in THF (1 M, 1.5 mL, 1.5 mmol) was added dropwise. The mixture was stirred at 20 °C for 2 h and then warmed to 55 °C, and stirred for an additional 8 h. The mixture was quenched with saturated aqueous NH_4Cl solution, extracted with ether (2×20 mL), and the organic phase was dried, concentrated in vacuo and chromatographed (hexane) to afford a brown oil which by GC–MS consists of a 1:10:1 **42/56/55** mixture (120 mg, 66%).

4.2.49. 5-*exo*-6-*endo*-Bis[(chloromethyl)sulfonyl]bicyclo[2.2.1]hept-2-ene (57). Freshly distilled cyclopentadiene (0.21 mL, 2.6 mmol) was added to a suspension of (*E*)-**7** (0.33 g, 1.3 mmol) in CH_2Cl_2 (4 mL) and the reaction mixture was stirred at room temperature until a colorless clear solution was obtained (ca. 10 min). Concentration in vacuo followed by chromatography of the residue afforded **57** as a colorless solid (0.35 g, 83%), mp 144–145 °C; IR (film) 1322 (SO_2), 1149 (SO_2), 1121 (SO_2) cm^{-1}; ^{1}H NMR δ 6.44 (dd, J=3.00, 5.4 Hz, 1H), 6.39 (dd, J=3.00, 5.4 Hz, 1H), 4.75 (d, J=8.4 Hz, 1H), 4.71 (d, J=8.4 Hz, 1H), 4.57 (d, J=12.6 Hz, 1H), 4.44 (dd, J=3.3, 5.1 Hz, 1H), 4.42 (d, J=12.6 Hz, 1H), 3.73 (dd, J=2.1, 5.1 Hz, 1H), 3.52 (m, 2H), 2.03 and 1.71 (AB_q, J=9.6 Hz, 2H); ^{13}C NMR δ 136.8, 136.2, 61.1, 60.5, 56.4, 56.2, 47.6, 46.6, 45.2. Anal. Calcd for $C_9H_{12}Cl_2O_4S_2$: C, 33.86; H, 3.79. Found: C, 33.51; H, 3.09.

4.2.50. 5-*endo*-6-*endo*-Bis[(chloromethyl)sulfonyl]bicyclo[2.2.1]hept-2-ene (58). Freshly distilled cyclopentadiene (0.1 mL, 1.2 mmol) was added to a suspension of (*Z*)-**7** (0.15 g, 0.6 mmol) in CH_2Cl_2 (4 mL) and the reaction mixture was stirred at room temperature until a clear colorless solution was obtained (ca. 10 min). The product was concentrated in vacuo and the residue chromatographed (hexanes/EtOAc 5:1) affording **58** as a colorless solid (0.16 g, 84%), mp 184–186 °C; IR (film) 1331 (SO_2), 1152 (SO_2) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 6.50 (m, 2H), 5.14 and 4.98 (AB_q, J=12.6 Hz, 4H), 4.79 (m, 2H), 3.82 (m, 2H), 1.76 and 1.65 (AB_q, J=9.0 Hz, 2H); ^{13}C NMR (CD_3COCD_3) δ 130.9, 60.3, 53.4, 43.7, 42.8. Anal. Calcd for $C_9H_{12}Cl_2O_4S_2$: C, 33.86; H, 3.79. Found: C, 33.72; H, 3.48.

4.2.51. 2-[(Chloromethyl)sulfonyl]bicyclo[2.2.1]hepta-2,5-diene (59). *Method* 1. A solution of KO*t*-Bu in THF (1.88 mL, 1.88 mmol, 1 M) was added to **57** (0.3 g, 0.94 mmol) in THF (10 mL) at 0 °C. The reaction mixture

was stirred at room temperature for 1 h and the reaction was quenched with NH_4Cl solution. The mixture was extracted with ether (2×20 mL), washed with brine (2×20 ml), dried, concentrated in vacuo and the residue chromatographed (hexanes/EtOAc 5:1, R_f=0.31) yielding **59** as a colorless oil (40 mg, 2%): ^{1}H NMR δ 7.84 (d, J=3.4 Hz, 1H), 6.97 (dd, J=3.2, 5.0 Hz, 1H), 6.79 (dd, J=3.2, 5.0 Hz, 1H), 4.40 and 4.36 (d, J=6.6 Hz, 2H), 3.94 (m, 1H), 3.87 (m, 1H), 2.35 and 2.23 (AB_q, J=7.2 Hz, 2H); ^{13}C NMR δ 161.5, 153.2, 142.9, 141.8, 75.4, 56.6, 52.3, 51.8; IR (neat) 1319, 1161 cm^{-1} (SO_2); EI-MS *m/z*: 204 (M^+, 14%), 154 (28%), 91 (100%), 65 (98%). *Method* 2. A solution of KO*t*-Bu in THF (0.62 mL, 0.62 mmol, 1 M) was added to **58** (0.1 g, 0.31 mmol) in THF (6 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h, quenched with NH_4Cl solution, extracted with ether (2×20 mL), washed with brine (2×20 ml), dried, concentrated in vacuo and the residue chromatographed (hexanes/EtOAc 5:1, R_f=0.31) yielding the title compound (10 mg, 16%). *Method* 3. [(Chloromethyl)sulfonyl]ethyne (**8**) (139 mg, 1.0 mmol) was placed in a 50 mL flask and cooled to 0 °C. Cyclopenta-1,3-diene (200 mg, 3.0 mmol) was added, then the mixture was stirred for 6 h at 0 °C. The reaction mixture was chromatographed (hexane/ethyl acetate=5:1) to yield **59** (186 mg, 91%) as a colorless oil. Compound **59** decomposes upon standing at room temperature.

4.2.52. 2-{2′,3′-Bis[(chloromethyl)sulfonyl]propyl}-6,6-dimethylbicyclo[3.1.1]hept-2-ene (61). A mixture of (*E*)-**7** (0.57 g, 2.25 mmol) and β-pinene (0.64 g, 4.67 mmol) in toluene (1.5 mL) were placed in a sealed tube and flushed with argon. The white slurry was heated at 135 °C for 1.5 h and then concentrated in vacuo at 60 °C and the residue chromatographed (hexanes/EtOAc 5:1) yielding **61** as a colorless solid (0.63 g, 72%), mp 108–110 °C; IR (film) 1323 (SO_2), 1122 (SO_2) cm^{-1}; ^{1}H NMR δ 5.09–5.51 (m, 1H), 4.63 and 4.77 (AB_q, J=12.6 Hz, 2H), 4.45 and 4.77 (AB_q, J=12.6 Hz, 2H), 4.01–4.13 (m, 2H), 3.29–3.35 (m, 1H), 2.74–2.82 (m, 1H), 2.40–2.50 (m, 2H), 2.26–2.28 (m, 2H), 2.01–2.12 (m, 2H), 1.88 (s, 3H), 1.15 (d, J=9 Hz, 1H), 0.83 (s, 3H); ^{13}C NMR δ 141.9, 123.1, 57.2, 55.9, 52.0, 47.6, 45.3, 40.3, 38.2, 36.5, 31.7, 31.5, 26.0, 21.1. Anal. Calcd for $C_9H_{12}Cl_2O_4S_2$: C, 43.29; H, 5.70. Found: C, 43.39; H, 5.78.

4.2.53. 2-[(3-Chloromethyl)sulfonylallyl]-6,6-dimethylbicyclo[3.3.1]hept-2-ene (62). A solution of KO*t*-Bu in THF (3.14 mL, 3.14 mmol, 1 M) was added to ene adduct **61** (0.61 g, 1.57 mmol) in THF (15 mL) at 0 °C and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with NH_4Cl solution, extracted with ether (2×20 mL), washed with H_2O (2×20 mL), dried, concentrated in vacuo and chromatographed (hexanes/EtOAc 5:1) to give (*E*)-2-buta-1,3-dienyl-6,6-dimethylbicyclo[3.3.1]hept-2-ene (**63**; see below) as a colorless oil (14 mg, 5%) and **62** (74 mg, 17%): IR (film) 1326 (SO_2), 1147 (SO_2), 1118 (SO_2) cm^{-1}; ^{1}H NMR δ 6.96 (ddd, J=15, 6.9, 7.2 Hz, 1H), 6.31 (d, J=15 Hz, 1H), 5.34 (m, 1H), 4.39 (s, 2H), 2.96 (d, J=6 Hz, 2H), 1.95–2.40 (m, 5H), 1.25 (s, 3H), 1.14 (d, J=8.7 Hz, 1H), 0.81 (s, 3H); ^{13}C NMR δ 151.4, 142.7, 125.6, 120.5, 57.3, 45.7, 40.6, 39.3, 38.2, 31.7, 31.4, 26.2, 21.2; GC *m/z* (rel. intensity) 276 (M^+, ^{37}Cl, 1), 274 (M^+, ^{35}Cl, 3), 117 (100), 91 (65), 77 (36).

4.2.54. (*E*)-2-Buta-1,3-dienyl-6,6-dimethylbicyclo[3.3.1]-hept-2-ene (63). A solution of KO*t*-Bu in THF (3.1 mL, 3.1 mmol, 1 M) was added to β-pinene adduct **61** (0.57 g, 1.46 mmol) in THF (30 mL) at 0 °C. The reaction mixture was refluxed for 1 h, quenched with NH_4Cl solution, and extracted with $CHCl_3$ (5×30 mL). The organic layer was washed with brine (2×30 mL) and dried, concentrated in vacuo and the residue chromatographed (hexanes) yielding **63** (30 mg, 12%) as a colorless oil: ^{1}H NMR δ 6.39 (dd, J=9.9, 16.8 Hz, 1H), 6.23 (d, J=15.6 Hz, 1H), 6.01 (d, J=15.6 Hz, 1H), 5.58 (s, 1H), 5.16 (d, J=16.8 Hz, 1H), 5.01 (d, J=9.9 Hz, 1H), 2.56 (m, 1H), 2.45–2.28 (m, 3H), 2.01 (m, 1H), 1.32 (s, 3H), 1.12 (d, J=8.7 Hz, 1H), 0.78 (s, 3H); ^{13}C NMR δ 146.5, 137.7, 134.6, 125.9, 125.5, 115.9, 41.0, 37.8, 32.2, 31.4, 29.7, 26.4, 21.1; GC/MS (rel. intensity) *m/z* 174 (M+, 10), 131 (44), 91 (100), 77 (41); UV (CH_2Cl_2) λ_{max} 278 nm.

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