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Chloromethanesulfonylethene and Dichloromethanesulfonylethene: New Reagents for Tandem Diels–Alder/Ramberg–Bäcklund Reactions

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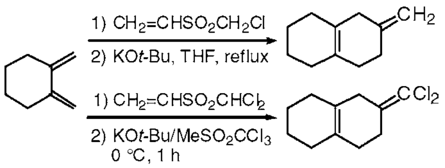
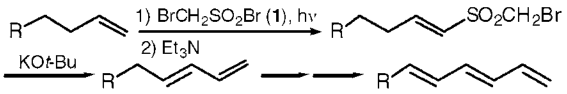
ABSTRACT



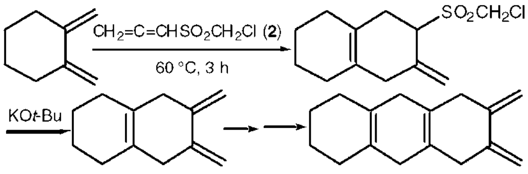
Chloromethanesulfonylethene (3a) and dichloromethanesulfonylethene (3b) were prepared by oxidation of the adducts of ethylene and $ClCH_2SCl$ or Cl_2CHSCl, respectively, followed by $NaHCO_3$ dehydrochlorination. With dienes, 3a gave Diels–Alder adducts that, with base, underwent Ramberg–Bäcklund reaction, giving products corresponding to the adducts of the dienes and allene. Similarly, 3b gave Diels–Alder adducts that, with base in the presence of the novel chlorine source $MeSO_2CCl_3$, cleanly afforded products corresponding to the adducts of the dienes and 1,1-dichloropropa-1,2-diene.

We have demonstrated the utility of bromomethanesulfonyl bromide ($BrCH_2SO_2Br$, **1**) in one-pot polyene syntheses via tandem reactions involving light-induced free-radical addition, dehydrobromination, and base-induced vinylogous Ramberg−Bäcklund reaction (Scheme 1).[1] We also showed that chloromethanesulfonyl-1,2-propadiene (CH_2═C═$CHSO_2CH_2Cl$, **2**) upon tandem Diels−Alder and Ramberg−Bäcklund reaction gives the formal Diels−Alder adducts of buta-1,2,3-triene (Scheme 2).[2] Do chloromethanesulfonylethene (CH_2═$CHSO_2CH_2Cl$, **3a**), dichloromethanesulfonylethene (CH_2═$CHSO_2CHCl_2$, **3b**), and 1,2-bis(chloromethanesulfonyl)ethene ($ClCH_2SO_2CH$═$CHSO_2CH_2Cl$, **4**) have similar utility as "prepackaged" Ramberg−Bäcklund reagents? Like **1** and **2**, **3a**,**b** and **4** have α-halogen and sulfonyl groups in place and, following an appropriate first step, might require only base to give the olefinic end products. We report

Scheme 1



Scheme 2



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[1] (a) Block, E.; Aslam, M. *J. Am. Chem. Soc.* **1983**, *105*, 6164. (b) Block, E.; Aslam, M.; Eswarakrishnan, V.; Wall, A. *J. Am. Chem. Soc.* **1983**, *105*, 6165. (c) Block, E.; Aslam, M.; Iyer, R.; Zubieta, J.; Hutchinson, J. *J. Org. Chem.* **1984**, *49*, 3664. (d) Block, E.; Eswarakrishnan, V.; Gebreyes, K. *Tetrahedron Lett.* **1984**, *25*, 5469. (e) Block, E.; Aslam, M.; Eswarakrishnan, V.; Gebreyes, K.; Hutchinson, J.; Iyer, R.; Laffitte, J.-A.; Wall, A. *J. Am. Chem. Soc.* **1986,** *108*, 4568. (f) Block, E.; Aslam, M. *Org. Synth.* **1987**, *65*, 90.

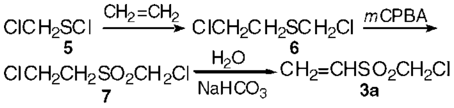
[2] Block, E.; Putman, D. *J. Am. Chem. Soc.* **1990**, *112*, 4072.

10.1021/ol0363523 CCC: $27.50

convenient syntheses of new reagents **3a**,**b** and (*E*,*Z*)-**4** and describe their utility as allene synthons in tandem processes involving Diels−Alder addition (or ene reaction) followed by Ramberg−Bäcklund rearrangement.[3]

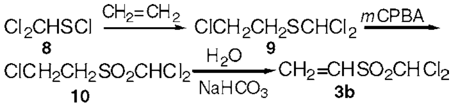
Chloromethanesulfenyl chloride, $ClCH_2SCl$, **5**, from reaction of Me_2S_2 with Cl_2,[4] serves as starting material for synthesis of **3a**,**b** and **4**. Treatment of **5** with ethylene gives 1-chloro-2-chloromethanesulfanylethane[5,6] (**6**; 90%), which without purification is oxidized with 2 equiv of *m*CPBA (giving **7** (not isolated)) and stirred with aqueous $NaHCO_3$ giving **3a** (99%), a colorless oil (Scheme 3).[7,8] A similar sequence of steps can be used to convert Cl_2CHSCl (**8**; from chlorination of **5**)[4] into **3b** (78%)[8] by way of 1-chloro-2-(dichloromethanesulfanyl)ethane (**9**) and 1-chloro-2-(dichloromethanesulfonyl)ethane (**10**) (neither isolated; Scheme 4).

Scheme 3



$$\underset{\mathbf{5}}{ClCH_2SCl} \xrightarrow{CH_2{=}CH_2} \underset{\mathbf{6}}{ClCH_2CH_2SCH_2Cl} \xrightarrow{mCPBA} \underset{\mathbf{7}}{ClCH_2CH_2SO_2CH_2Cl} \xrightarrow[NaHCO_3]{H_2O} \underset{\mathbf{3a}}{CH_2{=}CHSO_2CH_2Cl}$$

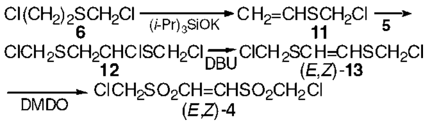
Scheme 4



$$\underset{\mathbf{8}}{Cl_2CHSCl} \xrightarrow{CH_2{=}CH_2} \underset{\mathbf{9}}{ClCH_2CH_2SCHCl_2} \xrightarrow{mCPBA} \underset{\mathbf{10}}{ClCH_2CH_2SO_2CHCl_2} \xrightarrow[NaHCO_3]{H_2O} \underset{\mathbf{3b}}{CH_2{=}CHSO_2CHCl_2}$$

Dehydrochlorination of **6** with $(i\text{-}Pr)_3SiOK$[9] gives chloromethanesulfanylethene (**11**; 69%),[8] which is converted to (*E*/*Z*)-1,2-bis-(chloromethanesulfonyl)ethene ((*E*/*Z*)-**4**)[8] by sequential addition of **5** (giving **12**; 96%), DBU dehydrochlorination of **12** to (*E*/*Z*)-**13** (58%; 1:3 E:Z), and oxidation with excess dimethyldioxirane (DMDO) (giving 28% (*E*)-**4** and 20% (*Z*)-**4**; Scheme 5).

Scheme 5

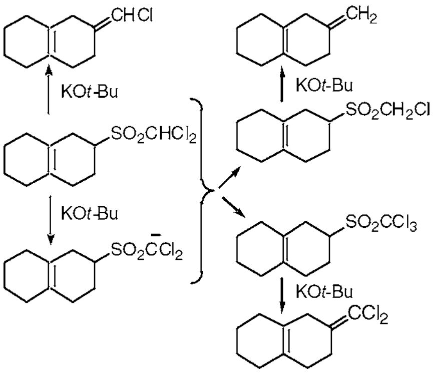


$$\underset{\mathbf{6}}{Cl(CH_2)_2SCH_2Cl} \xrightarrow[(i\text{-}Pr)_3SiOK]{} \underset{\mathbf{11}}{CH_2{=}CHSCH_2Cl} \xrightarrow[\mathbf{5}]{} \underset{\mathbf{12}}{ClCH_2SCH_2CHClSCH_2Cl} \xrightarrow[DBU]{} \underset{(E,Z)\text{-}\mathbf{13}}{ClCH_2SCH{=}CHSCH_2Cl} \xrightarrow[DMDO]{} \underset{(E,Z)\text{-}\mathbf{4}}{ClCH_2SO_2CH{=}CHSO_2CH_2Cl}$$

We examined the Diels−Alder reactivity of new compounds **3a** and **3b**, 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, and the experimental difficulties associated with gaseous reagents. Because of the above problems, a variety of allene synthons have been devised such as methanesulfonyl-α-bromoethene,[10a] α-bromoacrolein,[10b] 2-(benzenesulfinyl)-propene,[10c] ethenyl triphenylphosphonium bromide,[10d] α-methylene-*β*-propiolactone,[10e] and 2,3-(bis(benzenesulfonyl))-propene.[10f]

Both **3a** and **3b** readily add to a variety of 1,3-dienes giving high yields of the corresponding Diels−Alder adducts, as shown in Table 1.[11] As anticipated, treatment of the Diels−Alder adducts of **3a** with KO*t*-Bu/THF give good yields of the diene-allene adducts via Ramberg−Bäcklund reaction (entries 1−5). Analogous base treatment of adducts of **3b** 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. The latter two compounds are presumably formed by nucleophilic attack of the α-sulfonyl-α-chlorocarbanion of the Diels−Alder adduct of **3b** on the chlorine of a second adduct molecule (Scheme 6).

Scheme 6



We reasoned that if base treatment of Diels−Alder adducts of **3b** 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-

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(3) General review: Taylor, R. J. K.; Casy, G. *Org. React.* **2003**, *62*, 357.

(4) Douglass, I. B.; Norton, R. V.; Weichman, R. L.; Clarkson, R. B. *J. Org. Chem.* **1969**, *34*, 1803.

(5) Brintzinger, H.; Pfannstiel, K.; Koddebush, H.; Kling, K. E. *Chem. Ber.* **1950**, *83*, 87.

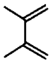
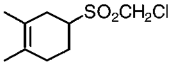
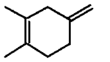
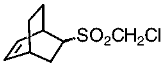
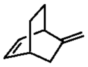
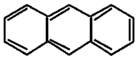
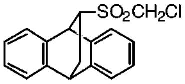
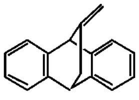
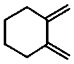
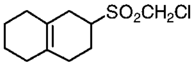
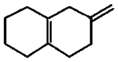
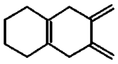
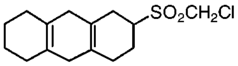
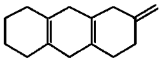
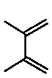
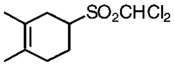
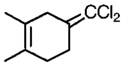
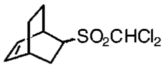
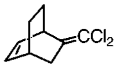
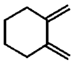
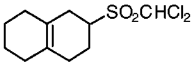
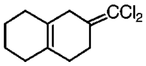
(6) *Caution*: *β*-Chlorosulfides may be toxic and should be handled in a hood using gloves; glassware should be rinsed with bleach after use.

(7) Related use of $NaHCO_3$: Iwamoto, R.; Kato, K.; Ikeuchi, S.; Suzuki, T. JP 2000063346, 2000; *Chem. Abstr.* **2000**, *132*, 180282.

(8) **3a**: ^1H NMR δ 6.69 (dd, $J = 9.7$, 16.5 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. **3b**: ^1H NMR δ 6.86 (dd, $J = 9.8$, 16.6 Hz, 1H), 6.69 (d, $J = 16.6$ Hz, 1H), 6.55 (d, $J = 9.7$ Hz, 1H), 6.26 (s, 1 H); ^{13}C NMR δ 78.7, 129.8, 137.3. (*E*)-**4**: mp 143−145 °C; IR 1389 (SO_2), 1124 (SO_2) cm^{-1}; ^1H NMR δ 7.82 (s, 2H), 5.22 (s, 4H), ^{13}C NMR δ 141.88, 57.19. (*Z*)-**4**: mp 113−115 °C; IR 1329 (SO_2), 1119 (SO_2) cm^{-1}; ^1H NMR δ 7.60 (s, 2H), 5.17 (s, 4H); ^{13}C NMR δ 141.80, 58.81 (NMR solvent: $CD_3C(O)CD_3$). **11**: ^1H NMR δ 6.39 (dd, $J = 9.9$, 16.9 Hz, 1H), 5.40 (dd, $J = 2.3$, 10.4 Hz, 1H), 5.39 (dd, $J = 2.4$, 16.6 Hz, 1H), 4.78 (*s*, 2H); ^{13}C NMR δ 129.0, 115.4, 47.8; GC-MS *m/z* (rel intensity) 110 (M^+, ^{37}Cl, 9), 108 (M^+, ^{35}Cl, 27), 73 (88), 46 (27), 45 (100). (*E*/*Z*)-**13**: bp 90−100 °C (0.02 Torr); ^1H 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* (rel intensity) 190 (M^+, ^{37}Cl, 33), 188 (M^+, ^{35}Cl, 45), 106 (93), 104 (100), 103 (70).

(9) Soderquist, J.; Vaquer, J.; Diaz, M.; Rane, A.; Bordwell, F.; Zhang, S. *Tetrahedron Lett.* **1996**, *37*, 2561.

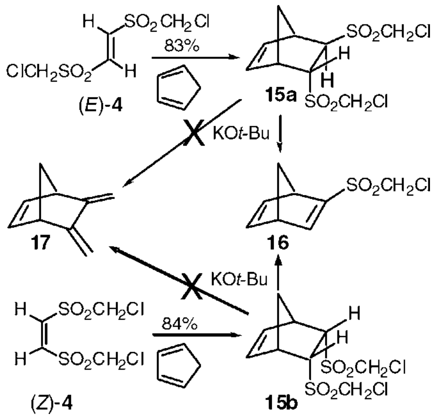
Table 1. Diels−Alder Adducts of **3a** and **3b** and the Corresponding Ramberg−Bäcklund Products

#	diene	Diels-Alder adduct	% yield	Ramberg-Bäcklund product	% yield
1			96^{d}		59^{c}
2			$95^{a,d}$		51^{c}
3			$96^{c,e}$		89^{c}
4			97^{d}		79
5			92^{f}		75
6			93^{d}		72
7			92^{b}		72
8			94^{d}		65

[a] Endo:exo = 6.3:1. [b] Endo:exo = 3:1. [c] Known compound.[10b] [d] Conditions: 100−130 °C, toluene, 12−16 h. [e] Conditions: 155 °C, toluene, 7 h. [f] Conditions: 60 °C, neat, 12 h.

dichloropropa-1,2-diene. To test this hypothesis, methyl trichloromethyl sulfone, $MeSO_2CCl_3$ (**14**), was used as a novel chlorine source. This little-studied compound[12] 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 **3b** were treated at 0 °C with KO*t*-Bu-THF in the presence of 2 equiv of **14**, the corresponding Diels−Alder adducts of 1,1-dichloropropa-1,2-diene were formed in good yield (Table 1, entries 6−8), despite concerns about competing sulfonate formation, often seen with 1,1,1-trichloromethyl sulfones.[3]

Scheme 7



Both (*E*)- and (*Z*)-**4** readily form Diels−Alder adducts, e.g., **15a** and **15b**, respectively, with 1,3-cyclopentadiene (Scheme 7), as confirmed by X-ray crystallography for **15a** (Figure 1), which also establishes the stereochemistry of (*E*)-**4**. Base treatment of **15a** or **15b** gave unstable 2-chloromethanesulfonylbicyclo[2.2.1]hepta-2,5-diene (**16**) rather than 5,6-bismethylenebicyclo[2.2.1]hept-2-ene (**17**), e.g., 1,2-elimination from the activated α-sulfonyl carbanions is favored over 1,3-elimination (Ramberg−Bäcklund reaction), even with the adduct of (*Z*)-**4**, where a coplanar 1,2-elimination transition state is impossible.[13]

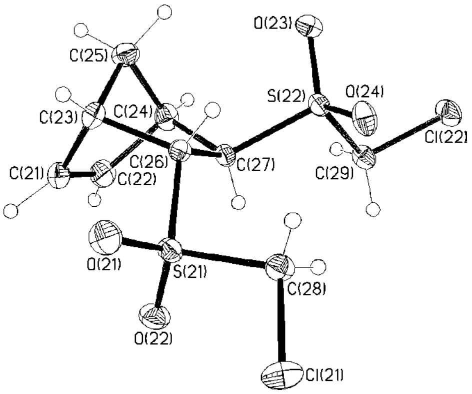
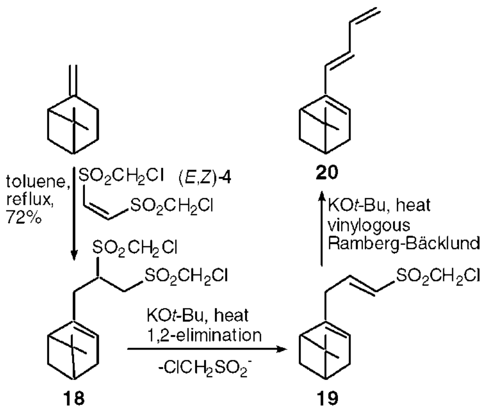


Figure 1. Structure of cyclopentadiene adduct **15a** of (*E*)-**4**.

Scheme 8



Since compound **4** showed good reactivity as a dienophile, we examined its reactivity in the ene reaction. When (*E*)-**4** was heated with 2 equiv of β-pinene in toluene at 135 °C for 1.5 h, the ene product 2-(1,2-bis(chloromethanesulfonyl)-ethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (**18**) was formed in 72% yield as a crystalline solid. Base treatment (*t*-BuOK) of **18** in refluxing THF afforded (*E*)-2-(buta-1,3-dienyl)-6,6-dimethylbicyclo[3.3.1]hept-2-ene (**20**) in low yield. If treatment with base was conducted at 0 °C, low yields of 2-(3-chloromethanesulfonylallyl)-6,6-dimethylbicyclo[3.3.1]hept-2-ene (**19**) could be isolated, leading to the overall proposed mechanism shown in Scheme 8. While not of synthetic utility due to low yield, the reaction in Scheme 8 represents the first example of a tandem reaction sequence incorporating an ene-reaction with Ramberg−Bäcklund elimination.

Acknowledgment. This work was supported by NSF (CHE-9906566 and CHE-01300985 [CCD X-ray diffractometer at SUNY−Albany]) and the Petroleum Research Fund, administered by the American Chemical Society.

Supporting Information Available: Representative experimental conditions, spectroscopic and analytical data for **3a**, **3b**, **4**, **11**, **13**, **18**, and Diels−Alder adducts and their Ramberg−Bäcklund rearrangement products, and X-ray structural data for **15a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) (a) Philips, J. C.; Oku, M. *J. Am. Chem. Soc.* **1972**, *94*, 1012. (b) Snider, B. B. *J. Org. Chem.* **1973**, *38*, 3961. (c) Williams, R. V.; Chauhan, K. *Chem. Commun.* **1991**, 1672. (d) Ruden, R. A.; Bonjouklian, R. *Tetrahedron Lett.* **1974**, *24*, 2095. Bonjouklian, R.; Ruden, R. A. *J. Org. Chem.* **1977**, *42*, 4095. (e) Adam, W.; Hasemann, L. *Tetrahedron Lett.* **1991**, *32*, 7033. (f) Padwa, A.; Kline, D. N.; Norman, B. H. *Tetrahedron Lett.* **1988**, *29*, 265.

(11) Mixtures of adducts were obtained with 2-substituted 1,3-dienes, e.g., myrcene (84%; 2.3:1 “para/meta” mixture [base treatment/aromatization gave mainly a para-disubstituted benzene]).

(12) Dronov, V. I.; Snegotskaya, V. A.; Ivanova, L. P.; Voronchikhina, D. P.; Bannikova, N. N. *Khim. Seraorg. Soedin., Soderzh. Neftyakh Nefteprod.* **1972**, *9*, 218; *Chem. Abstr.* **1973**, *79*, 115056.

(13) X-ray structure of **15a** shows SC(26)C(27)S and HC(26)C(27)H dihedral angles of −110.58(16) and 124(3)°, respectively. Similarly, cis isomer **15b** should have H on C(26) or C(27) far from syn or anti-periplanar with sulfur (see Supporting Information for details on X-ray structure).