γ-Lactone Formation in the Addition of Benzenesulfonyl Bromide to Diene and Enyne Esters

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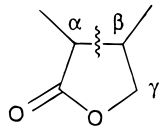
The gem-dialkyl effect has been used to promote the formation of functionalized γ-lactones in the addition of benzenesulfonyl bromide to diene and enyne esters. Introduction of 3 mol % of pyridine into the reactions increases the yields of lactones produced from tertiary esters. Formation of the $C_\alpha-C_\beta$ bond of γ-lactones has been achieved in both $C_\alpha \rightarrow C_\beta$ and $C_\beta \rightarrow C_\alpha$ radical cyclization directions.

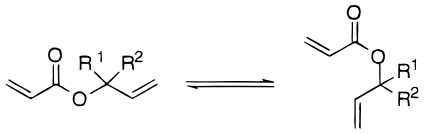
Introduction

The lactone skeleton exists in many bioactive natural products.[1] Functionalized lactones are important intermediates for the synthesis of stereo-defined acyclic and other natural products.[2] The synthesis of γ-lactones can be achieved by the lactonization of hydroxy acids, Baeyer−Villiger oxidation, the insertion of a carbonyl group by transition metals, etc.[3] In recent years, assembly of γ-lactones by formation of the $C_\alpha-C_\beta$ (or C_3-C_4) bond has drawn attention. Lu reported the Pd-catalyzed enyne cyclization as a convenient method to make α-alkylidene-γ-butyrolactone derivatives.[4] Also, radical cyclization methodology has been explored in this field. In most radical cyclization reports, a carbamoyl radical, generated from its α-derivative precursor, intramolecularly adds to a C=C or C≡C bond in a 5-exo mode.[5] However, the reactions generally proceed either in very low concentration or at high temperatures,[6] and functional groups are often lost.



The use of diene or enyne esters, such as allyl acrylates, as precusors to functionalized lactones is a promising route. However, the radical adduct of a diene ester (**1**, Y = CO) has a much slower rate of cyclization than that of a diene ether (**1**, Y = CH_2).[7] In fact, the addition of tosyl bromide to allyl acrylate affords only a low yield of acrylic C=C monoadduct along with other telomers or polymer (Scheme 1). This is partially because ester **1** (Y = CO) exists primarily in an s-trans conformation at room temperature, while the cyclization process requires an s-cis conformer.

It has been found that the addition of an arylsulfonyl halide to *N*-allyl acrylamides leads to lactams as long as the second alkyl substituent on the amide N is bulky enough to ensure the cyclization-required s-cis conformer.[8] Conformer population of diene esters can be influenced by the gem-dialkyl or Thorpe-Ingold effect.[9] Gem-dialkyl groups can increase the population of the s-cis conformer (**2** as R^1, R^2 are alkyl groups) and reduce the barrier for s-trans to s-cis interconversion.



2, s-trans **2**, s-cis

We have explored the possibility of using the gem-dialkyl effect to promote γ-lactone formation from diene and enyne esters. Since the sulfonyl group is a very versatile group in organic synthesis,[10] we have chosen $PhSO_2Br$ to initiate cyclization and thus incorporate sulfonyl and halide groups into the final lactones.

Results and Discussion

1. Addition of $PhSO_2Br$ to Acrylates. Table 1 summarizes the results of the addition of $PhSO_2Br$ to

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(1) (a) Drioli, S.; Felluga, F.; Forzato, C.; Nitti, P.; Pitacco, G.; Valentin, E. *J. Org. Chem.* **1998**, *63*, 2385. (b) Rossi, R.; Bellina, F.; Mannina, F. *Tetrahedron Lett.* **1998**, *39*, 3017. (c) Jacobi, P. A.; Herradura, P. *Tetrahedron Lett.* **1996**, *37*, 8297. (d) Rodriguez, C. M.; Martin, T.; Martin, V. S. *J. Org. Chem.* **1996**, *61*, 8448. (e) MacRae, W. D.; Towers, G. H. N. *Phytochemistry* **1984**, *23*, 1207.

(2) (a) Robin, S.; Huet, F.; Fuvw, A.; Veschambre, H. *Tetrahedron Asymmetry* **1993**, *4*, 239. (b) Hanessian, S.; Murray, P. J.; Sahoo, S. P. *Tetrahedron Lett.* **1985**, *26*, 5623. (c) Cossy, J.; Ranaivosata, J. L.; Bellosa, V. *Tetrahedron Lett.* **1994**, *35*, 1205. (d) Rojo, J.; Oarcia, M.; Carretero, J. C. *Tetrahedron* **1993**, *49*, 9787. (e) Koch, S. C.; Chamberlin, A. R. *J. Org. Chem.* **1993**, *58*, 2725. (f) Ribbons, D. W.; Sutherland, A. G. *Tetrahedron* **1994**, *50*, 3587. (g) Brown, H. C.; Kulkstni, S. V.; Rscherla, U. S. *J. Org. Chem.* **1994**, *59*, 365.

(3) Ogliaruso, M. A.; Wolfe, J. F. *Synthesis of Lactones and Lactams*; John Wiley & Sons: New York, 1993.

(4) (a) Lu, X.; Zhu, G.; Wang, Z.; Ma, S.; Ji, J.; Zhang, Z. *Pure Appl. Chem.* **1997**, *69*, 553. (b) Lu, X.; Zhu, G.; Wang, Z. *Synlett* **1998**, 117.

(5) (a) Clough, J. M.; Pattenden, G.; Wright, P. G. *Tetrahedron Lett.* **1989**, *30*, 7469. (b) Nagashima, H.; Seki, K.; Ozaki, N.; Wakamatsu, H.; Itoh, K.; Tomo, Y.; Tsuji, J. *J. Org. Chem.* **1990**, *55*, 985. (c) Russell, G. A.; Li, C.; Chen, P. *J. Am. Chem. Soc.* **1996**, *118*, 9831.

(6) (a) Hanessian, S.; Di Fabio, R.; Marcoux, J.-F.; Prud'homme, M. *J. Org. Chem.* **1990**, *55*, 3436. (b) Curran, D. P.; Tamine, J. *J. Org. Chem.* **1991**, *56*, 2746.

(7) Serra, A. C.; da Silva Correa, C. M. M.; do Vale, M. L. C. *Tetrahedron Lett.* **1991**, *47*, 9463.

(8) Riggi, I. D.; Gastaldi, S.; Jurzur, J.-M.; Bertrand, M. P. *J. Org. Chem.* **1992**, *57*, 6118.

(9) (a) Jung, M. E.; Gervoy, J. *J. Am. Chem. Soc.* **1991**, *113*, 224. (b) Jung, M. E.; Trifunovich, I. D.; Lensen, N. *Tetrahedron Lett.* **1992**, *33*, 6719.

(10) Chatgilialoglu, C. *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons Ltd.: New York, 1988; p 1089.

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Scheme 1

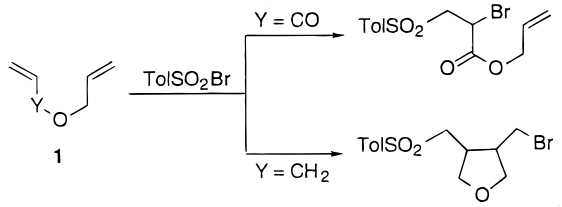


Table 1. Addition of $PhSO_2Br$ to Allyl Acrylates (2) under Sunlamp Irradiation in CH_3CN

2	R^1	R2	products (yield %)
2a	H	H	**5a** (15)
2b	Me	H	**5b** (23)
2c	Me	Me	**3c** (54, 74[a]) **6**[b](31)
2d	*i*-Pr	*i*-Pr	**3d** (30, 56[a])
2e	$-(CH_2)_5-$		**3e** (26, 55[a]) **7** (24) **8** (10)
2f	*t*-Bu	H	**3f** (18, 41[c]) **5f** (53, 15[c])
2g	$-CH=CH_2$	H	**5g** (23)

[a] Yields of the reactions with 3 mol % of pyridine. [b] Compound **6** is an inseparable mixture of **6a** and **6b** in a ratio of 1/4.[11] [c] Yields of the reaction diluted to 1/4 of the typical concentration.

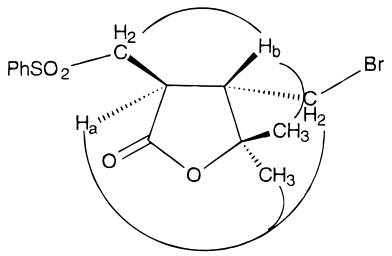
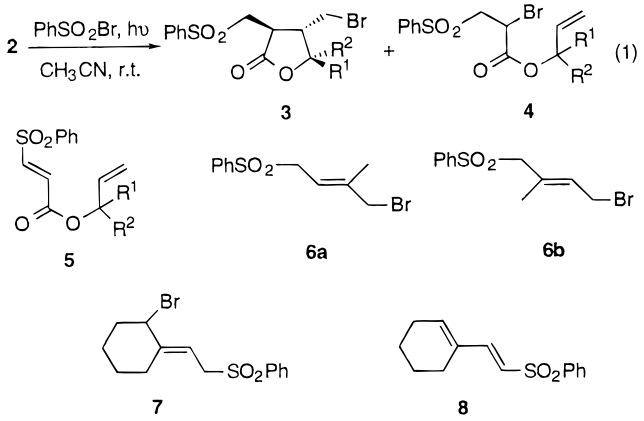


Figure 1. $^1H-^1H$ NOE of **3c**.

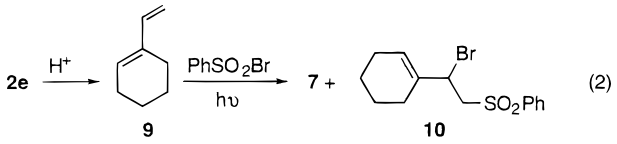
allyl acrylates **2** (eq 1). All reactions were conducted in acetonitrile under sunlamp irradiation at room temperature.



Uncyclized monoadducts **4** partially dehydrobrominated during TLC separation. Treatment of **4** with triethylamine at room temperature yielded sulfone **5** quantitatively.

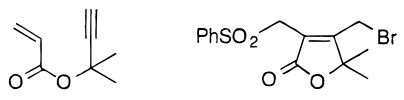
The results in Table 1 show that, with gem-dialkyl groups R^1 and R^2, γ-lactones can be formed stereoselectively from the diene esters. Only trans cyclized lactones **3c**−**f** were isolated. The configurations of the lactones were determined by 2D COSY and NOESY spectroscopy. Taking **3c** as an example, the assignment of its trans configuration is based on the observed NOE coupling shown in Figure 1. No NOE was observed between $PhSO_2C\mathbf{H_2}$ and $BrC\mathbf{H_2}$. The NOE coupling between the two methine H's (H_a and H_b) cannot be used as a criterion, because of their close distance in both cis and trans configurations. Another possible structure with the groups $PhSO_2$ and Br reversed in **3c** was excluded by HMBC (heteronuclear multiple bond correlation) 2D spectroscopy. In the HMBC spectrum, H_a correlates to $\mathbf{C}{=}O$ (δ 173.00 ppm) and $PhSO_2\mathbf{C}H_2$ (δ 56.63 ppm), while H_b correlates to $-\mathbf{C}Me_2$ (δ 85.85 ppm) and $Br\mathbf{C}H_2$ (δ 29.38 ppm).

Products **6**, **7**, and **8** come from the addition of $PhSO_2$-Br to dienes liberated from the corresponding tertiary esters. Since the $PhSO_2Br$ sample inevitably contains a trace of acid, the R^1 and R^2 groups facilitate the acid-catalyzed hydrolysis and dehydration of the tertiary esters. We have found that the addition of 3 mol % of pyridine to the reaction mixture increases the yields of **3c**−**e** to 74%, 56%, and 55%, respectively, with the decreased yields of **6**, **7**, and **8**. We have also confirmed that isoprene was generated when **2c** was mixed with $PhSO_2Br$ and kept in the dark at 40 °C for 1 h. The addition of $PhSO_2Br$ to an authentic isoprene sample under the same reaction conditions yielded 93% of **6** with the same ratio of **6a**/**6b**. Similarly, **7** and **8** come from the addition of $PhSO_2Br$ to olefin **9**, which was liberated from **2e** (eq 2). Since **10** and **3e** are inseparable on TLC, the mixture was treated with triethylamine for 1 h at room temperature, and then **8** and **3e** could be separated.



One interesting product is lactone **3f** from ester **2f**. Only one stereoisomer was found with the *t*-Bu group trans to $-CH_2Br$ and cis to $-CH_2SO_2Ph$. The chiral center at the γ-position induces the configurations of both α and β chiral centers in one step. Though the yield of **3f** was only 18%, it could be increased to 41% when the concentration of the reaction mixture was diluted to one-fourth of that used in Table 1, and the yield of **5f** was decreased to 15%. Obviously, a reaction conducted at low concentration favors intramolecular cyclization.

The addition of $PhSO_2Br$ to acrylate **11** yielded lactone **12** in 40%. The gem-dimethyl groups were found essential for the formation of lactone **12**, and an isomerization step of the C=C bond was involved.[5a]

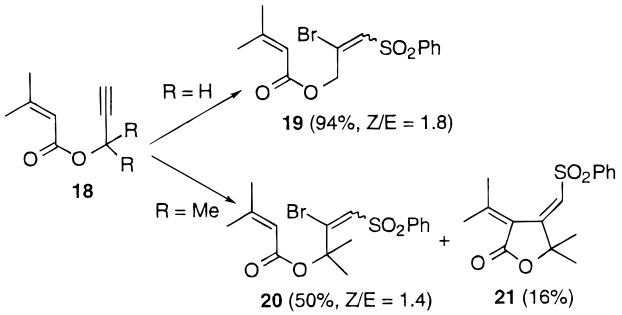


It is interesting to note that all of the lactones mentioned thus far are formed by radical cyclizations proceeding from C_α to C_β. The sulfonyl radical always adds preferentially to the acrylic C=C bond than the allyl C=C bond or propargyl C≡C bond, even though it is an electrophilic radical[12] and the acrylic C=C bond is more electrophilic. Another electrophilic radical $Cl_3C^\bullet$, gener-

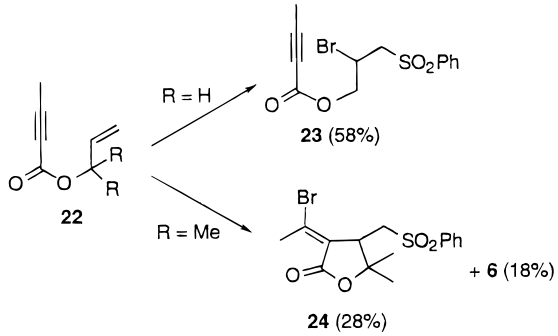
(11) Zakharkin, L. I.; Zhigareva, G. G. *J. Org. Chem. USSR* **1973**, 918.

(12) (a) Takahara, Y.; Lino, M.; Matsuda, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2268. (b) da Silva Correa, C. M. M.; Waters, W. A. *J. Chem. Soc., Perkins Trans. 2* **1972**, 1575.

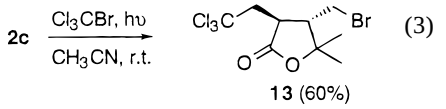
Scheme 2



Scheme 3



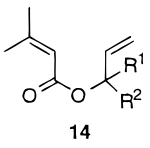
ated from Cl_3CBr under photolysis, also gave the $C_\alpha \rightarrow C_\beta$ cyclized lactone **13** (eq 3). This shows that polar effects do not control the chemoselectivity of the radical addition step here.



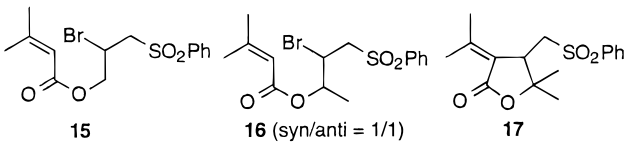
(3)

2. Addition of $PhSO_2Br$ to β-Substituted Acrylates and Propiolates. Assembling the lactone skeleton with different functionality by a $C_\beta \rightarrow C_\alpha$ cyclization process can be achieved with β-substituted acrylates and propiolates.

The addition of $PhSO_2Br$ to diene esters **14a** and **14b** yielded uncyclized **15** (68%) and **16** (65%), respectively. The addition of $PhSO_2Br$ to ester **14c** yielded lactone **17** (65%) and **6** (10%), which also shows the gem-dimethyl effect in the $C_\beta \rightarrow C_\alpha$ radical cyclization process. However, no significant reactions were observed for esters **14d**−**f** even after prolonged reaction times. This suggests that a bulky R^1 or R^2 group strongly inhibits the addition of $PhSO_2^\bullet$ to the allyl C═C bond or the bromo-transfer from $PhSO_2Br$ to the adduct radicals. The reversibility of this addition step is predominant when the rate of the $C_\beta \rightarrow C_\alpha$ cyclization step is slow. This inhibition effect is similar to the steric effect introduced by remotely positioned groups[13] and can explain the chemoselectivity shown in Table 1. The reversible addition of sulfonyl radicals to C═C bonds has been observed in many cases.[14]

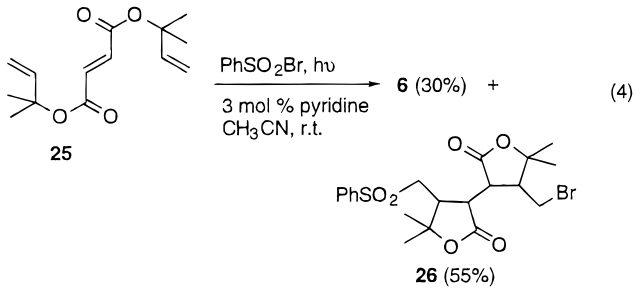


14	R^1	R^2
a	H	H
b	H	Me
c	Me	Me
d	H	*t*-Bu
e	H	Ph
f	H	2,4,6-$Me_3C_6H_2$



Gem-dialkyl groups can also promote $C_\beta \rightarrow C_\alpha$ cyclization in the addition of $PhSO_2Br$ to enyne esters **18** and **19** (Schemes 2 and 3). It is unexpected that both **21** and **24** were isolated as only one stereoisomer, whose configurations were determined by 2D NOESY spectroscopy.

So far, both $C_\alpha \rightarrow C_\beta$ and $C_\beta \rightarrow C_\alpha$ cyclizations have been observed separately. They can proceed in sequence as in the addition of $PhSO_2Br$ to fumarate **25**. Compound **26** was isolated as a mixture of stereoisomers in a yield of 33%, and its yield was increased to 55% when 3 mol % pyridine was added before photolysis (eq 4).



(4)

Conclusion

Our work shows that the gem-dialkyl effect can be used to promote γ-lactone formation in the addition of $PhSO_2Br$ to diene and enyne esters. This effect is more significant for diene esters than for enyne esters. Also, gem-dialkyl groups strongly inhibit the addition of $PhSO_2^\bullet$ to the allyl C═C bond of allyl acrylates or allyl propiolates and facilitate the hydrolysis and dehydration of tertiary esters. Introduction of 3 mol % of pyridine as a base into the reactions increases the yields of lactones produced from tertiary esters.

Experimental Section

NMR spectra were recorded in $CDCl_3$ unless stated otherwise (^1H at 400 MHz and ^{13}C at 100 MHz). IR spectra were measured as thin films on a NaCl plate. All melting points were determined without correction. Photostimulated reactions utilized a 275 W fluorescent sunlamp. Yields are based on the starting esters. $PhSO_2Br$ was prepared according to a literature procedure.[15] Esters **2a**,**b**, **2f**,**g**, **14a**,**b**, **14d**−**f**, **18** (R = H), and **22** (R = H) were prepared from the appropriate acyl chlorides and alcohols with triethylamine at room temperature in anhydrous ethyl ether. Esters **2c**−**e**, **11**, **14c**, **18** (R = Me), **22** (R = Me), and **25** were prepared from the appropriate acyl chlorides and deprotonated alcohols (by *n*-BuLi) at 0 °C in anhydrous ethyl ether.

General Procedure for the Addition of $PhSO_2Br$ to Diene or Enyne Esters. A mixture of the ester (0.20 mmol) and $PhSO_2Br$ (0.22 mmol) with or without 3 mol % of pyridine in CH_3CN (1.0 mL) was irradiated in a 5 mm NMR tube at

(13) (a) Huyser, E. S.; Taliaferro, J. O. *J. Org. Chem.* **1963**, *28*, 1676. (b) Bridger, R. F.; Russell, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754.

(14) (a) Kuehne, M. E.; Pamon, R. E. *J. Org. Chem.* **1977**, *42*, 1825. (b) Edwards, J. E.; McQuillin, F. J.; Wood, M. *J. Org. Chem.* **1978**, *43*, 438. (c) Stork, G.; Mook, R. *J. Am. Chem. Soc.* **1987**, *109*, 2829. (d) Smith, T. A. K.; Whitham, G. H.; *J. Chem. Soc., Chem. Commun.* **1985**, 897.

(15) Poshkus, A. C.; Herweh, J. E.; Magnotta, F. A. *J. Org. Chem.* **1963**, *28*, 2766.

room temperature until the starting ester disappeared as indicated by TLC analysis. The products were obtained by TLC separation on 20 × 10 cm silica gel plates with hexanes−ethyl acetate as the eluent.

***trans*-3-Benzenesulfonylmethyl-4-bromomethyl-5,5-dimethyldihydro-2(3*H*)-furanone (3c)** was isolated as a white solid, mp 123−125 °C: IR (cm^{-1}) 1770, 1308, 1146; ^1H NMR δ 1.46 (s, 3H), 1.68 (s, 3H), 2.76 (ddd, J = 4.0, 11.0, 11.7 Hz, 1H), 3.09 (ddd, J = 3.0, 7.8, 11.7 Hz, 1H), 3.28 (dd, J = 7.8, 14.4 Hz, 1H), 3.45 (t, J = 11.0 Hz, 1H), 3.79 (dd, J = 3.0, 14.4 Hz, 1H), 4.18 (dd, J = 4.0, 11.0 Hz, 1H), 7.60−8.00 (m, 5H); ^{13}C NMR δ 21.93, 28.60, 29.55, 40.76, 52.37. 56.81, 86.03, 128.15, 129.82, 134.60, 139.24, 173.18; HREIMS m/z (relative intensity) 281.0848 [8, calcd for $C_{14}H_{17}O_2S$ (M − Br) 281.0848], 263 (27), 223 (19), 148 (100), 139 (34), 125 (59), 123 (46), 95 (93), 77 (49); CIMS m/z 380/378 (M + NH_4^+).

***trans*-3-Benzenesulfonylmethyl-4-bromomethyl-5,5-diisopropyldihydro-2(3*H*)-furanone (3d)** was isolated as a colorless oil: IR (cm^{-1}) 1770, 1319, 1152; ^1H NMR δ 0.97 (d, J = 6.8 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H), 1.04 (d, J = 6.8 Hz, 3H), 1.06 (d, J = 6.8 Hz, 3H), 2.22 (septet, J = 6.8 Hz, 1H), 2.38 (septet, J = 6.8 Hz, 1H), 3.16 (ddd, J = 5.2, 6.0, 7.2 Hz, 1H), 3.23 (ddd, J = 4.8, 5.2, 6.0 Hz, 1H), 3.52 (dd, J = 5.2, 14.4 Hz, 1H), 3.68 (dd, J = 5.2, 10.8 Hz, 1H), 3.80 (dd, J = 4.8, 14.4 Hz, 1H), 3.90 (dd, J = 7.2, 10.8 Hz, 1H), 7.50−8.10 (m, 5H); ^{13}C NMR δ 17.10, 17.12, 17.77, 19.44, 30.83, 31.17, 33.23, 43.71, 44.98, 57.06, 93.25, 128.22, 129.63, 134.31, 139.91, 174.41; HREIMS m/z (relative intensity) 373.0117 [8, calcd for $C_{15}H_{18}{}^{79}BrO_4S$ (M − C_3H_7) 373.0109], 293 (100), 275 (19), 223 (13), 151 (83), 125 (24), 77 (30), 41 (48); CIMS m/z 436/334 (M + NH_4^+).

***trans*-3-Benzenesulfonylmethyl-4-bromomethyl-1-oxaspiro[4,5]-2-decanone (3e)** was isolated as a white solid, mp 205−207 °C: IR (cm^{-1}) 1761, 1310, 1148; ^1H NMR δ 1.20−1.30 (m, 2H), 1.55−1.90 (m, 7H), 2.10−2.20 (m, 1H), 2.68 (ddd, J = 4.0, 10.0, 11.6 Hz, 1H), 3.11 (ddd, J = 3.2, 7.6, 11.6 Hz, 1H), 3.31 (dd, J = 7.6, 14.4 Hz, 1H), 3.52 (dd, J = 10.0, 11.2 Hz, 1H), 3.78 (dd, J = 3.2, 14.4 Hz, 1H), 4.09 (dd, J = 4.0, 11.2 Hz, 1H), 7.60−8.00 (m, 5H); ^{13}C NMR δ 21.55, 22.72, 25.16, 28.75, 30.80, 38.21, 40.55, 52.41, 56.90, 87.25, 128.17, 129.79, 134.55, 139.30, 173.49; HREIMS m/z (relative intensity) 321.1168 [58, calcd for $C_{17}H_{21}O_4S$ (M − Br) 321.1161], 303(18), 259 (17), 223 (41), 179(100), 125 (51), 77 (69), 69 (81), 55 (43), 53 (46); CIMS m/z 420/418 (M + NH_4^+).

(3α, 4*β*, 5α)-(±)-3-Benzenesulfonylmethyl-4-bromomethyl-5-*tert*-butyldihydro-2(3*H*)-furanone (3f) was isolated as a white solid, mp 103−105 °C: IR (cm^{-1}) 1771, 1309, 1154; ^1H NMR δ 1.01 (s, 9H), 2.81−2.86 (m, 1H), 3.23 (dd, J = 10.8, 14.0 Hz, 1H), 3.37 (ddd, J = 2.4, 7.2, 10.8 Hz, 1H), 3.62 (dd, J = 2.8, 10.2 Hz, 1H), 3.72 (dd, J = 2.4, 14.0 Hz, 1H), 4.21 (dd, J = 2.8, 10.2 Hz, 1H), 4.25 (d, J = 6.4 Hz, 1H), 3.90 (dd, J = 7.2, 10.8 Hz, 1H), 7.60−8.00 (m, 5H); ^{13}C NMR δ 25.40, 34.78, 37.57, 39.69, 41.36, 56.99, 89.51, 128.26, 129.89, 134.68, 138.60, 174.95; HREIMS m/z (relative intensity) 331.9726 [62, calcd for $C_{12}H_{13}{}^{79}BrO_4S$ (M − C_4H_8) 331.9718], 225 (10), 197 (16), 151 (15), 143 (78), 125 (84), 109 (46), 77 (49), 57 (100); CIMS m/z 408/406 (M + NH_4^+).

(*E*)-1-Benzenesulfonyl-2-methyl-4-bromo-2-butene (6a) and (*E*)-1-Benzenesulfonyl-3-methyl-4-bromo-2-butene (6b). Compound **6** was isolated as an inseparable white solid mixture of **6a** and **6b** in a ratio of 1/4 (from ^1H NMR), mp 70−72 °C (lit.[11] 73−74 °C). The NMR data were obtained from mixture of sulfone **6**. **6a**: ^1H NMR δ 1.86 (s, 3H), 3.77 (s, 2H), 3.85 (d, J = 8.4 Hz, 2H), 5.39 (t, J = 8.4 Hz, 1H), 7.27−7.87 (m, 5H); ^{13}C NMR δ 16.92, 26.96, 65.74, 128.71, 129.38, 130.39, 130.65, 134.05, 138.24; **6b**: ^1H NMR δ 1.43 (s, 3H), 3.82 (d, J = 8.0 Hz, 2H), 3.88 (s, 2H), 5.62 (t, J = 8.4 Hz, 1H), 7.27−7.87 (m, 5H); ^{13}C NMR δ 14.94, 38.92, 56.18, 116.46, 128.67, 129.47, 134.05, 138.46, 141.89; HREIMS of **6** m/z (relative intensity) 209.0639 [100, calcd for $C_{11}H_{13}O_2S$ (M − Br) 209.0636], 145 (14), 125 (24), 77 (66), 53 (15); CIMS m/z 308/306 (M + NH_4^+).

3-Benzenesulfonylmethyl-4-bromomethyl-5,5-dimethyl-2(5*H*)-furanone (12) was isolated as a white solid, mp 162−164 °C: IR (cm^{-1}) 1758, 1310, 1144; ^1H NMR δ 1.56 (s, 6H), 4.25 (s, 2H), 4.38 (s, 2H), 7.50−7.90 (m, 5H); ^{13}C NMR δ 18.87, 25.46, 51.48, 86.92, 119.59, 128.62, 129.60, 134.83, 138.06, 168.87, 169.59; HREIMS m/z (relative intensity) 279.0687 [75, calcd for $C_{14}H_{15}SO_4$ (M − Br) 279.0691), 215 (48), 125 (18), 123 (64), 121 (47), 95 (20), 77 (82), 67 (20), 51 (41), 42 (100).

***trans*-4-Bromomethyl-3-(2,2,2-trichloroethyl)-5,5-diisopropyldihydro-2(3*H*)-furanone (13)** was isolated as a white solid, mp 119−121 °C: IR (cm^{-1}) 1770; ^1H NMR δ 1.49 (s, 3H), 1.68 (s, 3H), 2.62 (dt, J = 4.0, 11.2 Hz, 1H), 2.80 (dt, J = 11.2, 4.4 Hz, 1H), 2.91 (dd, J = 4.4, 15.2 Hz, 1H), 3.42 (t, J = 11.2 Hz, 1H), 3.50 (dd, J = 4.4, 15.2 Hz, 1H), 3.87 (dd, J = 4.0, 11.2 Hz, 1H); ^{13}C NMR δ 21.60, 28.53, 29.58, 43.93, 52.72. 54.42, 85.13, 97.84, 173.95; HREIMS m/z (relative intensity) 320.8843 [7, calcd for $C_8H_9{}^{79}Br{}^{35}Cl_3O_2S$ (M − CH_3) 320.8852), 267 (5), 201 (26), 199 (28), 135 (39), 117 (100), 75 (45); CIMS m/z 360/358/356/354 (M + NH_4^+).

4-Benzenesulfonylmethyl-3-isopropylidene-5,5-dimethyldihydro-2(3*H*)-furanone (17) was isolated as a white solid, mp 143−144 °C: IR (cm^{-1}) 1743, 1308, 1150; ^1H NMR δ (CD_3CN) 1.32 (s, 3H), 1.43 (s, 3H), 1.73 (s, 3H), 2.10 (s, 3H), 3.14 (dd, J = 3.2, 15.2 Hz, 3H), 3.38−3.41 (m, 1H), 3.63 (dd, J = 8.0, 15.2 Hz, 1H), 7.60−7.90 (m, 5H); ^{13}C NMR δ 20.76, 23.71, 24.01, 29.75, 43.11, 57.79, 81.78, 124.56, 128.02, 129.83, 134.34, 140.03, 153.66, 168.51; HREIMS m/z (relative intensity) 308.1080 (36, calcd for $C_{16}H_{20}SO_4$ 308.1082), 290 (9), 225 (7), 166 (63), 149 (62), 121 (80), 81 (100), 43 (35).

4-(*E*)-Benzenesulfonylmethylene-3-isopropylidene-5,5-dimethyldihydro-2-(3*H*)-furanone (21) was isolated as a white solid, mp 135−137 °C: IR (cm^{-1}) 1756, 1307, 1150; ^1H NMR δ 1.40 (s, 6H), 2.37 (s, 3H), 2.51 (s, 3H), 6.04 (s, 1H), 7.50−7.90 (m, 5H); ^{13}C NMR δ 22.67, 26.60, 28.40, 82.84, 121.43, 127.50, 129.52, 131.59, 133.78, 141.26, 152.63, 165.88, 167.80; HREIMS m/z (relative intensity) 306.0923 [24, calcd for $C_{16}H_{18}SO_4$ 306.0926), 288 (14), 165 (100), 147 (15), 119 (23), 77 (59), 43 (36).

4-Benzenesulfonylmethyl-3-(*E*)-(1-bromo)ethylidene-5,5-dimethyldihydro-2(3*H*)-furanone (24) was isolated as an inseparable mixture with **6**: ^1H NMR δ 1.50 (s, 3H), 1.70 (s, 3H), 2.80 (s, 3H), 3.31 (dd, J = 1.0, 14.8 Hz, 1H), 3.51 (d, J = 10.0 Hz, 1H), 3.59 (dd, J = 10.0, 14.8 Hz, 1H), 7.60−7.90 (m, 5H); ^{13}C NMR δ 24.13, 26.20, 30.22, 48.38, 56.22, 82.76, 128.35, 129.70, 129.73, 134.30, 142.00, 142.76, 165.21; HREIMS m/z (relative intensity) 293.0845 [100, calcd for $C_{15}H_{17}SO_4$ (M − Br) 293.0848], 209 (3), 175 (14), 125 (17), 107 (17), 77 (23); CIMS m/z 392/390 (M + NH_4^+).

4-Benzenesulfonylmethyl-3-[4′-bromomethyl-5′,5′-dimethyldihydro-2′(3′*H*)-furanone-3′-yl)]-5,5-dimethyldihydro-2(3*H*)-furanone (26) was isolated as a mixture of stereoisomers. Only one isomer can be isolated partially pure as a white solid, mp 165−167 °C: IR (cm^{-1}) 1766, 1307, 1109. ^1H NMR δ 1.29 (s, 3H), 1.40 (s, 3H), 1.46 (s, 3H), 1.68 (s, 3H), 3.14−3.58 (m, 8H), 7.60−8.00 (m, 5H); ^{13}C NMR δ 21.90, 23.09, 27.13, 28.34, 29.56, 41.19, 44.51, 44.62, 48.73, 56.40, 84.49, 85.49, 128.35, 129.92, 134.69, 138.70, 174.53, 174.63; HREIMS m/z (relative intensity) 472.0554 [8, calcd for $C_{20}H_{25}SO_6{}^{79}Br$ 472.0555], 393 (100), 251 (40), 233 (32), 193 (17), 125 (20), 77 (60), 69 (75), 43 (65); CIMS m/z 490 (M + NH_4^+).

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Supporting Information Available: Characterization data for compounds **5a**, **5b**, **5f**, **5g**, **7**, **8**, **15**, **16**, **19**, **20**, and **23**; ^1H, ^{13}C NMR and 2D $^1H-^1H$ NOE spectra for compounds **3c**−**f**, **13**, and **21**; ^1H and ^{13}C spectra for compounds **5b**, **5f**, **6**−**8**, **12**, **15**−**17**, **19**, **20**, and **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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