Synthesis of Symmetrical Sulfones from Rongalite: Expansion to Cyclic Sulfones by Ring-Closing Metathesis

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A simple method for the synthesis of symmetrical sulfones using rongalite has been developed. Terminally olefinic sulfone derivatives were subjected to ring-closing metathesis (RCM) reactions to generate cyclic sulfones.

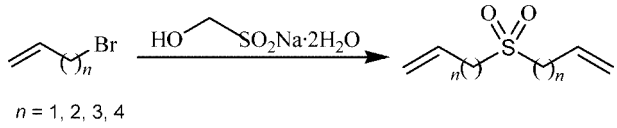
Introduction

Sulfones are useful synthons for the construction of carbon–carbon bonds via anionic, cationic, and radical intermediates.[1] Fused or 3-substituted sulfolenes are a latent source of conjugated dienes. Therefore, they are useful partners in Diels–Alder reactions for the synthesis of complex synthetic targets containing six-membered rings.[2] Due to the electron-withdrawing nature of the sulfone moiety, neighboring methylene or methyl group(s) can be alkylated with various electrophiles. This unique reactivity coupled with the ease of desulfonylation has been exploited in several instances for the construction of various theoretically interesting and biologically active molecules.[3] Moreover, α-halogenated sulfones are valuable precursors for the Ramberg–Bäcklund reaction.[4] In view of the varied applications, sulfone derivatives are the preferred starting materials for diversity-oriented synthesis.

Although sulfones are used widely in organic synthesis,[5] most of the methods involve multistep synthetic sequences.[6] The importance of sulfones encouraged us to search for alternate synthetic routes. In this context, we identified rongalite as a readily available source of the sulfoxylate dianion. Rongalite (trade name for sodium hydroxymethanesulfinate or sodium formaldehydesulfoxylate) is commonly used in the textile industry as a decolorizing agent. Although there are few reports demonstrating the utility of rongalite as a source of SO_2^{2-},[7] it has remained dormant in synthetic organic chemistry.

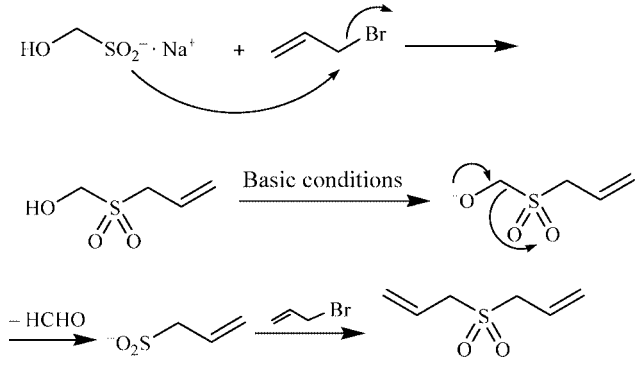
Results and Discussion

Herein we report our preliminary results for the synthesis of symmetrical sulfones in a one-pot procedure. For example, the open chain, terminal-olefin-containing symmetrical sulfones (**7**–**10**), were conveniently prepared by treating various alkyl bromides of different chain length with an excess amount of rongalite in the presence of potassium carbonate and the phase-transfer catalyst (PTC) tetrabutylammonium bromide (Scheme 1).



Scheme 1.

The possible mechanism for the formation of sulfone derivatives is shown in Scheme 2. The reaction involves nucleophilic displacement by the hydroxymethanesulfinate anion, followed by the loss of a formaldehyde molecule in the presence of a base, thus generating a nucleophile for the second alkylation step.



Scheme 2. Proposed mechanism for the formation of sulfone derivatives.

To test the feasibility of this methodology in intramolecular systems, 1,8-bis(bromomethyl)naphthalene (**5**) was treated with rongalite and potassium carbonate under PTC

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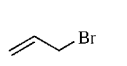
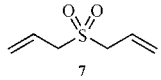
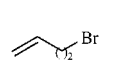
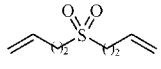
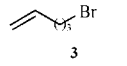
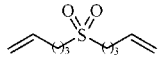
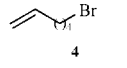
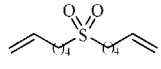
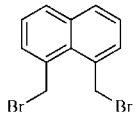
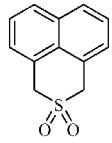
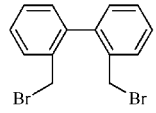
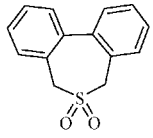
conditions. We were pleased to obtain the corresponding sulfone **11** in good yield. Subsequently, under the same reaction conditions, 2,2′-bis(bromomethyl)-1,1′-biphenyl (**6**) gave the corresponding sulfone **12**. Various sulfone derivatives prepared are listed in Table 1.

Table 1. Sulfone derivatives prepared from rongalite.

Entry	Starting halide	Conditions	Sulfone derivative	Yield
1	 **1**	K_2CO_3,TBAB, DMF, 72 h, r.t.	 **7**	50%
2	 **2**	K_2CO_3,TBAB, DMF, 72 h, r.t.	 **8**	54%
3	 **3**	K_2CO_3,TBAB, DMF, 72 h, r.t.	 **9**	59%
4	 **4**	K_2CO_3, TBAB, DMF, 72 h, r.t.	 **10**	61%
5	 **5**	K_2CO_3,TBAB, DMF, 24 h, r.t.	 **11**	75%
6	 **6**	K_2CO_3,TBAB, DMF, 24 h, r.t.	 **12**	98%

Acyclic sulfones **7**–**10** appear to be ideal candidates for the synthesis of cyclic sulfone derivatives by the ring-closing metathesis (RCM) reaction. In recent years, metathesis[8,9] has emerged as a powerful synthetic tool for the construction of various carbo-, hetero- and macrocyclic compounds. The ruthenium–carbene catalysts **A**[10] and **B**[11] (Figure 1), developed by Grubbs and coworkers, have attracted a great deal of attention due to their broad functional group tolerance.

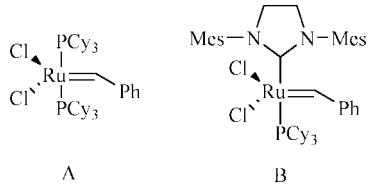
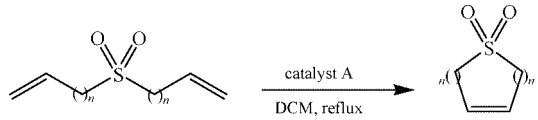


Figure 1. Ruthenium-based olefin metathesis catalysts.

The compatibility of sulfonamide and sulfamide functionalities with ruthenium-based catalysts is well-established.[12,13] However, applications of RCM for the synthesis of cyclic sulfones are relatively rare.[14] The diallyl sulfone **7** was treated with Grubbs catalyst **A** in refluxing dichloromethane to give a 97% isolated yield of the butadiene sulfone **13**. Along similar lines, sulfone **14** was obtained in 97% yield starting with **8** (Scheme 3).

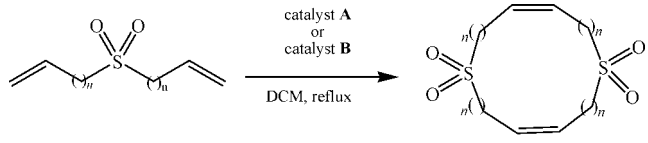


	n
7	1
8	2

	n	yield
13	1	97%
14	2	97%

Scheme 3.

To our surprise, the RCM reaction of the sulfone derivative **9** with both the catalysts **A** and **B** gave a diastereomeric mixture of the 18-membered macrocyclic bis-sulfone **15**. This dimer was found to be sparingly soluble in ethyl acetate. All attempts to purify the product by column chromatography resulted in poor recovery. Eventually, the difference in solubility of the macrocyclic bis-sulfone in ethyl acetate and chloroform was exploited for its purification. A short pad of silica gel was charged with the crude reaction mixture and washed with chloroform. The washings were concentrated, and the residue obtained after the removal of chloroform was rinsed with a cold ethyl acetate/petroleum ether mixture (10:1) two to three times to remove trace impurities of the catalyst. The purified product was obtained in moderate yield. Subsequently, the diastereomeric mixture of the 22-membered macrocyclic bis-sulfone **16** was obtained, starting with **10**, in a similar manner (Scheme 4).



	n
9	3
10	4

	n	catalyst A	catalyst B
15	3	31%	60%
16	4	42%	33%

Scheme 4.

In view of the less favorable free-energy changes associated with the formation of 9- and 11-membered rings, the hypothetical ligating interactions between the sulfonyl oxy-

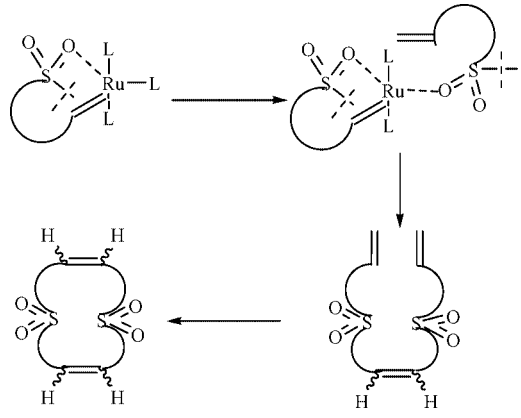


Figure 2. Possible mechanism for the formation of sulfone dimers.

gens and the ruthenium center[15] can account for the formation of dimers. The structural rigidity induced by this chelating effect may be responsible for the formation of one of the diastereomers as the major product (Figure 2).

Conclusion

We believe that this method should serve as a useful addition to the existing methods for the synthesis of sulfones. Overall, a simple and economical procedure has been developed for the synthesis of symmetrical sulfone derivatives, and this protocol should find its way in organic synthesis for carbon–carbon-bond-forming reactions. Efforts are underway in our laboratory towards the expansion of the chemistry described here.

Experimental Section

General Remarks: Analytical TLC was performed on (10 × 5 cm) glass plates coated with silica gel G or GF 254 (containing 13% $CaSO_4$ as a binder). Visualization of the spot on the TLC plate was achieved by exposure to either I_2 vapor or UV light. Flash chromatography was performed using silica gel (100–200 mesh), and the column was usually eluted with an EtOAc/ petroleum ether (b.p. 60–80 °C) mixture. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectroscopic data were recorded with Varian VXR 300 or 400 MHz spectrometers using TMS as the internal standard and $CDCl_3$ as the solvent. The coupling constants (*J*) are given in Hertz (Hz). 1st Generation (**A**) and 2nd Generation (**B**) Grubbs catalysts were purchased from Strem and Fluka chemicals, respectively. Allyl bromide and tetrabutylammonium bromide were purchased from the Loba Chemical Company, India, and allyl bromide was freshly distilled before use. *N*,*N*′-dimethylformamide was purchased from Merck. For all the reactions anhydrous Na_2SO_4 was used as drying agent after workup. 4-Bromo-1-butene, 5-bromo-1-pentene and 6-bromo-1-hexene were purchased from Lancaster and 1,8-bis(bromomethyl)naphthalene and 2,2′-bis(bromomethyl)-1,1′-biphenyl were purchased from Aldrich. All commercial grade reagents were used without further purification. Infrared spectra were recorded with a Nicolet 400 FT IR spectrometer in KBr/CH_2Cl_2, and the absorptions are reported in cm^{-1}. The high-resolution mass measurements were carried out using either a JEOL JMS-DX 303 GC-MS or a Q-Tof Micro (YA-105)-Micromass UK instrument.

Preparation of Compound 7: A suspension of rongalite (3.85 g, 25 mmol), potassium carbonate (3.45 g, 25 mmol), tetrabutylammonium bromide (80.5 mg, 0.25 mmol), and allyl bromide **1** (600 mg, 5 mmol) in DMF (25 mL) was stirred at room temperature for 72 h and then quenched with cold water (15 mL). The aqueous phase was extracted with diethyl ether (3 × 50 mL). The organic layer was washed with water and brine, dried with anhydrous sodium sulfate, and concentrated. The crude compound was purified by silica gel column chromatography. Elution of the column with a 10% ethyl acetate/petroleum ether mixture gave the diallyl sulfone **7** (184 mg, 50%) as a colorless liquid. IR (neat): $\tilde{\nu}_{max}$ = 1650, 1433, 1321, 1137, 939 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.70–3.72 (d, J = 8 Hz, 4 H), 5.42–5.46 (dd, J = 16.8, J = 1.2 Hz, 2 H), 5.51–5.53 (d, J = 10 Hz, 2 H), 5.88–5.98 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 56.1, 125.0, 125.1 ppm. HRMS: *m*/*z*: $(M + 1)^+$ found 147.0485; calcd. for $C_6H_{11}O_2S$ 147.0480.

Preparation of Compound 8: A suspension of rongalite (1.73 g, 11.23 mmol), potassium carbonate (1.55 g, 11.23 mmol), tetrabutylammonium bromide (35 mg, 0.11 mmol), and 4-bromo-1-butene **2** (300 mg, 2.25 mmol) in DMF (25 mL) was stirred at room temperature for 72 h and then quenched with cold water (15 mL). The aqueous phase was extracted with diethyl ether (3 × 50 mL). The organic layer was washed with water and brine, dried with anhydrous sodium sulfate, and concentrated. The crude compound was purified by silica gel column chromatography. Elution of the column with a 10% ethyl acetate/petroleum ether mixture gave the compound **8** (106 mg, 54%) as a colorless liquid. IR (neat): $\tilde{\nu}_{max}$ = 1643, 1446, 1321, 1137, 926 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.57–2.63 (m, 4 H), 3.03–3.07 (m, 4 H), 5.11–5.19 (m, 4 H), 5.77–5.87 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.2, 52.3, 117.7, 134.0 ppm. HRMS: *m*/*z*: $(M + 1)^+$ found 175.0798; calcd. for $C_8H_{15}O_2S$ 175.0793.

Preparation of Compound 9: A suspension of rongalite (1.54 g, 10.00 mmol), potassium carbonate (1.38 g, 10.00 mmol), tetrabutylammonium bromide (32 mg, 0.1 mmol), and 5-bromo-1-pentene **3** (300 mg, 2.01 mmol) in DMF (25 mL) was stirred at room temperature for 72 h and then quenched with cold water (15 mL). The aqueous phase was extracted with diethyl ether (3 × 50 mL). The organic layer was washed with water and brine, dried with anhydrous sodium sulfate, and concentrated. The crude compound was purified by silica gel column chromatography. Elution of the column with a 10% ethyl acetate/petroleum ether mixture gave the compound **9** (120 mg, 59%) as a colorless solid having a low melting point. IR (KBr): $\tilde{\nu}_{max}$ = 1647, 1459, 1280, 1133, 1000, 914 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91–1.98 (m, 4 H), 2.19–2.24 (m, 4 H), 2.93–2.97 (m, 4 H), 5.05–5.10 (m, 4 H), 5.71–5.81 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.1, 32.3, 52.1, 116.8, 136.4 ppm. HRMS: *m*/*z*: $(M + 1)^+$ found 203.1101; calcd. for $C_{10}H_{19}O_2S$ 203.1106.

Preparation of Compound 10: A suspension of rongalite (1.41 g, 9.15 mmol), potassium carbonate (1.2 g, 8.69 mmol), tetrabutylammonium bromide (29 mg, 0.09 mmol), and 6-bromo-1-hexene **4** (300 mg, 1.84 mmol) in DMF (25 mL) was stirred at room temperature for 72 h and then quenched with cold water (15 mL). The aqueous phase was extracted with diethyl ether (3 × 50 mL). The organic layer was washed with water and brine, dried with anhydrous sodium sulfate, and concentrated. The crude compound was purified by silica gel column chromatography. Elution of the column with a 10% ethyl acetate/petroleum ether mixture gave the compound **10** (128 mg, 61%) as a solid having a low melting point. IR (KBr): $\tilde{\nu}_{max}$ = 1652, 1479, 1316, 1133, 995, 919 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51–1.67 (m, 4 H), 1.81–1.92 (m, 4 H), 2.08–2.14 (m, 4 H), 2.90–2.97 (m, 4 H), 4.98–5.06 (m, 4 H), 5.72–5.83 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.5, 27.8, 33.2, 52.6, 115.6, 137.6 ppm. HRMS: *m*/*z*: $(M + 1)^+$ found 231.1422; calcd. for $C_{12}H_{23}O_2S$ 231.1419.

Preparation of Compound 11: A suspension of rongalite (123 mg, 0.80 mmol), potassium carbonate (110 mg, 0.80 mmol), tetrabutylammonium bromide (26 mg, 0.08 mmol), and 1,8-bis(bromomethyl)naphthalene **5** (50 mg, 0.16 mmol) in DMF (5 mL) was stirred at room temperature for 24 h and then quenched with cold water (15 mL). The aqueous phase was extracted with diethyl ether (3 × 50 mL). The organic layer was washed with water and brine, dried with anhydrous sodium sulfate, and concentrated. The crude compound was purified by silica gel column chromatography. Elution of the column with a 4% ethyl acetate/petroleum ether mixture gave the compound **11** (24 mg, 75%) as a colorless solid. M.p.: 242 °C (Ref.[16] 240–242 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.57

(s, 4 H), 7.30–7.32 (m, 2 H), 7.44–7.49 (m, 2 H), 7.82–7.85 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.4, 126.1, 127.1, 128.0, 129.3, 134.4 ppm.

Preparation of Compound 12: A suspension of rongalite (115 mg, 0.75 mmol), potassium carbonate (103 mg, 0.75 mmol), tetrabutylammonium bromide (24 mg, 0.075 mmol), and 2,2′-bis(bromomethyl)-1,1′-biphenyl **6** (50 mg, 0.15 mmol) in DMF (5 mL) was stirred at room temperature for 24 h and then quenched with cold water (15 mL). The aqueous phase was extracted with diethyl ether (3 × 50 mL). The organic layer was washed with water and brine, dried with anhydrous sodium sulfate, and concentrated. The crude compound was purified by silica gel column chromatography. Elution of the column with a 4% ethyl acetate/petroleum ether mixture gave the compound **12** (35 mg, 98%) as a colorless solid. M.p.: 210–211 °C (Ref.[17] 209–210 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.03 (s, 4 H), 7.49–7.52 (m, 8 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 57.4, 128.1, 129.0, 129.4, 129.5, 130.6, 139.9 ppm.

Preparation of Compound 13: To a solution of sulfone **7** (18 mg, 0.123 mmol) in dry dichloromethane (6 mL) was added Grubbs 1st Generation catalyst **A** (1.97 mg, 0.0024 mmol, 2 mol-%), and the reaction mixture was heated to reflux under nitrogen for 4 h. Then, the reaction mixture was cooled to room temperature and concentrated to dryness under vacuum. The crude compound was purified by silica gel column chromatography. Elution of the column with a 15% ethyl acetate/petroleum ether mixture gave the 2,5-dihydrothiophene 1,1-dioxide (**13**) (14 mg, 97%) as a colorless crystalline solid. M.p.: 63–64 °C (Ref.[18] 64–65.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 4 H), 6.08 (s, 2 H) ppm.

Preparation of Compound 14: To a solution of sulfone **8** (70 mg, 0.402 mmol) in dry dichloromethane (10 mL) was added Grubbs 1st Generation catalyst **A** (11.1 mg, 0.013 mmol, 3.33 mol-%), and the reaction mixture was heated to reflux under nitrogen for 3 h. Then, the reaction mixture was cooled to room temperature and concentrated to dryness. The crude compound was purified by silica gel column chromatography. Elution of the column with a 20% ethyl acetate/petroleum ether mixture gave the compound **14** (57 mg, 97%) as a colorless crystalline solid. M.p.: 88–90 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3037, 2972, 1688, 1455, 1341, 1313, 1276, 1211, 1199, 1109 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.48–2.54 (m, 4 H), 2.96–3.00 (m, 4 H), 5.96–6.06 (m, 2 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.1, 53.4, 131.5 ppm. HRMS: *m/z*: $(M + Na)^+$ found 169.0292; calcd. for $C_6H_{10}O_2SNa$ 169.0299.

Preparation of Compound 15: To a solution of sulfone **9** (25 mg, 0.123 mmol) in dry dichloromethane (5 mL) was added Grubbs 2nd Generation catalyst **B** (2 mg, 0.0024 mmol, 2 mol-%), and the reaction mixture was heated to reflux under nitrogen for 4 h. Then, the reaction mixture was cooled to room temperature and concentrated to dryness. A short pad of silica gel was charged with the crude reaction mixture and washed with chloroform (30 mL). The washings were concentrated, and the residue obtained after the removal of chloroform was rinsed with a small amount of cold ethyl acetate/petroleum ether mixture (10:1) two to three times to remove trace impurities of the catalyst. The colorless solid **15** obtained (13 mg, 60%) was found to be sparingly soluble in ethyl acetate but showed good solubility in chloroform and dichloromethane. IR (KBr): $\tilde{\nu}_{max}$ = 3001, 2923, 1651, 1455, 1305, 1288, 1248, 1133, 1113 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85–1.95 (m, 8 H), 2.00–2.25 (m, 8 H), 2.86–2.98 (m, 8 H), 5.05–5.48 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.3, 30.5, 51.2, 130.7 (major diastereomer) ppm. HRMS: *m/z*: $(M + 1)^+$ found 349.1506; calcd. for $C_{16}H_{29}O_4S_2$ 349.1507.

Preparation of Compound 16: To a solution of sulfone **10** (28 mg, 0.121 mmol) in dry dichloromethane (5 mL) was added Grubbs 2nd Generation catalyst **B** (2 mg, 0.0024 mmol, 2 mol-%), and the reaction mixture was heated to reflux under nitrogen for 4 h. Then, the reaction mixture was cooled to room temperature and concentrated to dryness under vacuum. A short pad of silica gel was charged with the crude reaction mixture and washed with chloroform (30 mL). The washings were concentrated, and the residue obtained after the removal of chloroform was rinsed with a small amount of cold ethyl acetate/petroleum ether mixture (10:1) two to three times to remove the trace impurities of the catalyst. The colorless solid **16** obtained (8 mg, 33%) was found to be sparingly soluble in ethyl acetate but showed good solubility in chloroform and dichloromethane. IR (KBr): $\tilde{\nu}_{max}$ = 2992, 2944, 1623, 1468, 1309, 1276, 1125, 1142, 1076 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42–1.58 (m, 8 H), 1.76–1.86 (m, 8 H), 2.06–2.08 (m, 8 H), 2.89–2.98 (m, 8 H), 5.30–5.42 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.5, 27.5, 31.3, 52.1, 130.6 (major diastereomer) ppm. HRMS: *m/z*: $(M + 1)^+$ found 405.2134; calcd. for $C_{20}H_{37}O_4S_2$ 405.2133.

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[1] a) E. N. Prilezhaeva, *Russ. Chem. Rev.* **2001**, *70*, 897–920; b) T. G. Back, *Tetrahedron* **2001**, *57*, 5263–5301; c) R. Chinchilla, C. Nájera, *Chem. Rev.* **2000**, *100*, 1891–1928; d) C. Nájera, J. M. Sansano, *Recent Res. Devel. Org. Chem.* **1998**, *2*, 637–683; e) R. Chinchilla, C. Nájera, *Recent Res. Devel. Org. Chem.* **1997**, *1*, 437–467; f) N. S Simpkins, *Sulphones in Organic Synthesis* Pergamon, Oxford, U.K., **1993**.

[2] a) F. Fringuelle, A. Taticchi, *The Diels–Alder Reaction. Selected Practical Methods*, John Wiley & Sons, New York, **2002**; b) A. Sandulache, A. M. S. Silva, J. A. S. Cavaleiro, *Tetrahedron* **2002**, *58*, 105–114; c) A. P. A. Crew, R. C. Storr, M. Yelland, *Tetrahedron Lett.* **1990**, *31*, 1491–1494.

[3] C. Nájera, M. Yus, *Tetrahedron* **1999**, *55*, 10547–10658.

[4] L. A. Paquette, *Org. React.* **1977**, *25*, 1–71.

[5] K. Tanaka, A. Kaji in *The Chemistry of Sulphones and Sulphoxides* (Eds.: S. Patai, Z. Rappoport, C. Stirling), John Wiley & Sons, New York, **1988**, pp. 729–821.

[6] K. Shank in *The Chemistry of Sulphones and Sulphoxides* (Eds.: S. Patai, Z. Rappoport, C. Stirling), John Wiley & Sons, New York, **1988**, pp. 165–231.

[7] a) A. R. Harris, T. J. Mason, *Synth. Commun.* **1989**, *19*, 529–535; b) A. Loupy, J. Sansoulet, A. R. Harris, *Synth. Commun.* **1989**, *19*, 2939–2946; c) A. Harris, *Synth. Commun.* **1988**, *18*, 659–663; d) W. F. Jarvis, M. D. Hoey, A. L. Finoccnio, D. C. Dittmer, *J. Org. Chem.* **1988**, *53*, 5750–5756; e) A. Harris, *Synth. Commun.* **1987**, *17*, 1587–1592.

[8] R. H. Grubbs, *Handbook of Metathesis*, Wiley-VCH, Weinheim, **2003**.

[9] Recent reviews: a) A. Deiters, S. F. Martin, *Chem. Rev.* **2004**, *104*, 2199–2238; b) M. D. McReynolds, J. M. Dougherty, P. R. Hanson, *Chem. Rev.* **2004**, *104*, 2239–2258; c) R. R. Schrock, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2003**, *42*, 4592–4633; d) S. Kotha, N. Sreenivasachary, *Indian J. Chem.* **2001**, *40B*, 763–780; e) A. Fürstner, *Angew. Chem. Int. Ed.* **2000**, *39*, 3012–3043.

[10] a) P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110; b) P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039–

2041; c) Z. Wu, S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1995**, *117*, 5503–5511.
[11] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.
[12] a) J.-D. Moriggi, L. J. Brown, J. L. Castro, R. C. D. Brown, *Org. Biomol. Chem.* **2004**, *2*, 835–844; b) J. Wanner, A. M. Harned, D. A. Probst, K. W. C. Poon, T. A. Klein, K. A. Snelgrove, P. R. Hanson, *Tetrahedron Lett.* **2002**, *43*, 917–921; c) R. C. D. Brown, J. L. Castro, J.-D. Moriggi, *Tetrahedron Lett.* **2000**, *41*, 3681–3685; d) D. D. Long, A. P. Termin, *Tetrahedron Lett.* **2000**, *41*, 6743–6747; e) C. Lane, V. Snieckus, *Synlett* **2000**, 1294–1296; f) P. R. Hanson, D. A. Probst, R. E. Robinson, M. Yau, *Tetrahedron Lett.* **1999**, *40*, 4761–4764; g) M. Ahmed, A. G. M. Barrett, D. C. Braddock, S. M. Cramp, P. A. Procopiou, *Tetrahedron Lett.* **1999**, *40*, 8657–8662.
[13] a) J. H. Jun, M. S. Jiménez, J. M. Dougherty, P. R. Hanson, *Tetrahedron* **2003**, *59*, 8901–8912; b) A. M. Harned, S. Mukherjee, D. L. Flynn, P. R. Hanson, *Org. Lett.* **2003**, *5*, 105–107; c) S. S. Salim, R. K. Bellingham, B. Satcharoen, R. C. D. Brown, *Org. Lett.* **2003**, *5*, 3403–3406; d) J. M. Dougherty, D. A. Probst, R. E. Robinson, J. D. Moore, T. A. Klein, K. A. Snelgrove, P. R. Hanson, *Tetrahedron* **2000**, *56*, 9781–9790.
[14] a) Q. Yao, *Org. Lett.* **2002**, *4*, 427–429; b) J. F. Miller, A. Termin, K. Koch, A. D. Piscopio, *J. Org. Chem.* **1998**, *63*, 3158–3159.
[15] L. A. Paquette, F. Fabris, J. Tae, J. C. Gallucci, J. E. Hofferberth, *J. Am. Chem. Soc.* **2000**, *122*, 3391–3398.
[16] J. Nakayama, E. Ohshima, H. M. Ishii, *J. Org. Chem.* **1983**, *48*, 60–65.
[17] M. Iovu, V. Radulescu, M. Iqbal, *Revue Roumaine de Chimie* **1985**, *30*, 713–717.
[18] N. J. Rahway, *The Merck Index*, 11th ed. (Ed.: S. Budavari), Merck & Co., Inc., U.S.A., **1989**, p. 8941.

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