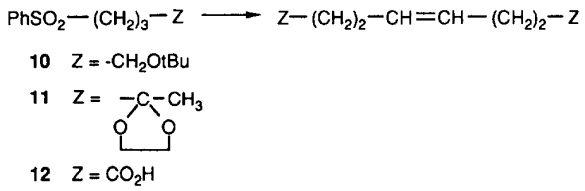
It should be pointed out that the formation of sulfone **19** from heptyl sulfone **7** is a catalytic process, like the formation of the symmetrical alkenes. The metal salt triggers the reaction which proceeds without consuming anything other than the sulfonyl carbanion.

Homocoupling of sulfones bearing functional groups

The nickel-promoted coupling reaction proved to be compatible with a few functional groups, provided the α-sulfonyl carbanion is stable: indeed those carbanions bearing a leaving group (halogen, phenoxy) may undergo an easy cyclization, independently of the presence of nickel catalyst. This is illustrated by the quantitative formation of phenyl cyclobutyl and phenyl cyclopropyl sulfones when 4-bromobutyl and 3-phenoxypropyl phenyl sulfones were lithiated and treated with nickel acetylacetonate.

On the other hand, 4-*tert*-butoxybutyl phenyl sulfone **10** or the protected ketosulfone **11** gave the corresponding dimeric alkenes in fair to good yields. In the latter case, slightly harder conditions had to be used, due to the poor solubility of the lithiated sulfone. Even the dianion of 4-(phenylsulfonyl)butanoic acid **12** could be converted into the corresponding carboxylic diacid. In each case, the stereochemistry of the carbon carbon double bond formed was approximately 50:50.



10 $Z = -CH_2OtBu$

11 $Z =$

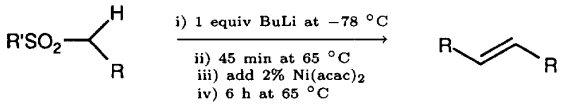
12 $Z = CO_2H$

Alkyl sulfones substituted in the α-position by an alkylthio substituent underwent the coupling reaction. Methylthiomethyl phenyl sulfone **13** gave (50%) 1,2-bis(methylthio)ethene. 1-(Methylthio)nonyl phenyl sulfone **14** gave only 15% of 9,10-bis(methylthio)octadec-9-ene together with 15% of 1-(methylthio)non-1-ene formed by elimination. It is known that elimination in these 1-(alkylthio)alkyl sulfones is very easily promoted by base [20a].

Homocoupling of metallated *tert*-butyl alkyl sulfones

The primary alkyl *tert*-butyl sulfones proved more reactive than the corresponding aryl-derivatives as shown in table V. Under the preceding reaction conditions *tert*-butyl *n*-pentyl and *tert*-butyl *n*-heptyl sulfone gave higher yields that the corresponding phenyl sulfones; the configuration of the resulting alkene was 50:50 instead of E/Z = 30:70. A smaller amount of starting sulfone (12–13%) was recovered and this was shown (by quenching with D_2O) to have been reprotonated which explains why the reaction stopped. At room temperature the *tert*-butyl sulfones already underwent the coupling reaction; a good yield (85%) being obtained after

Table V. Comparison of phenyl pentyl **8** or heptyl **7** sulfones and their *tert*-butyl analogs **8a** and **7a** at 65 °C.



	R'-SO₂-CH₂R R	*RCH=CHR* % (E/Z)[a]	*Sulfone recovered (%)*
8	n-C_4H_9	63 (28:72)	10
8a	n-C_4H_9	75	12
7	n-C_6H_{13}	60 (30:70)	30
7a	n-C_6H_{13}	76 (44:56)	12

[a] GLC.

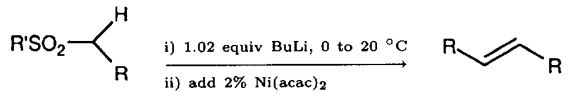
16 h. The stereoselectivity E/Z was now 30:70 as in the case of the aryl sulfone (table VI). A number of primary alkyl sulfones gave very similar results.

As some unchanged reprotonated sulfone was still present at the end of the reaction, more base was used. The amount of unchanged sulfone indeed decreased but so did the yield of dimeric alkene whereas a larger amount of material could not be accounted for (see table VII). With an excess of organolithium, another reaction took place, which was shown to be a nickel-promoted elimination leading to the alkene with the same carbon skeleton: higher alkyl sulfones such as *tert*-butyl dodecyl sulfone **9a** led to the less volatile dodecene which could be detected.

t-Bu SO_2-CH_2-CH_2-$C_{10}H_{21}$ + 1.5 equiv BuLi
⟶ dodecenes 65%

Partial isomerization of the initially formed terminal alkene took place in this medium. However, it was possible to work out conditions leading to a clean elimination process [21], a valuable result since base-promoted

Table VI. Comparison of phenyl dodecyl **9**, heptyl **7** and pentyl **8** sulfones and their *tert*-butyl analogs **9a**, **7a** and **8a** at room temperature.



Sulfone	*R*	*Reaction time (h)*	*Alkene* (E/Z)	*Recovered sulfone (%)*
9	n-$C_{11}H_{23}$	18	40[a]	50
9	n-$C_{11}H_{23}$	48	60	–
9	n-$C_{11}H_{23}$	91	69 (27:73)	10
9a	n-$C_{11}H_{23}$	18	90[b] (36:64)	4
7	n-C_6H_{13}	90	65	12
7a	n-C_6H_{13}	16	85 (31:69)	8
8	n-C_4H_9	90	62	12
8a	n-C_4H_9	18	81	8

[a] GLC; [b] isolated.

Table VIII. Homocoupling of *tert*-butyl *sec*-alkyl sulfones in THF (2% $Ni(acac)_2$).

Sulfone	*T (°C)*	t *(h)*	*Homocoupling (%) GLC*	*Elimination (%) GLC*	*Recovered sulfone (%)*
t-$BuSO_2CHBuHex$	25	24	30	$C_{11}H_{22}$[a] 10	50
	65	6	25	$C_{11}H_{22}$[a] 55	8
t-$BuSO_2CHHex_2$	25	24	36	$C_{13}H_{26}$[b] 12	40
	65	6	30	$C_{13}H_{26}$[b] 50	10
t-$BuSO_2CHMePen$	65	6	25	–	–
$PhSO_2CHMeHex$	25	24	10	–	–

[a] Mixture of Hex-CH=CH-Pr and Pen-CH=CH-*n*-Bu; [b] Hex-CH=CH-Pen.

elimination in sulfones is usually an extremely sluggish reaction which takes place efficiently only when double bonds (C=C or C=O) are to be conjugated with the newly formed one.

Table VII. Influence of the amount of base on the homocoupling of *tert*-butyl heptyl sulfone **7a** (2% $Ni(acac)_2$ 16 h, in THF at rt).

Equiv BuLi	*Dimeric alkene (%)* (E/Z)	*Sulfone recovered (%)*
1	84 (28:72)	8
1.1	70 (51:49)	4
1.2	60 (49:51)	2

A number of secondary sulfones were also treated under the same reaction conditions, ie, one equivalent of organolithium and nickel acetylacetonate (2%) at room temperature or 65 °C.

The homocoupling did take place leading to tetrasubstituted alkenes in about 30% yield. However competitive elimination now also happened even without excess of base. The monomeric alkenes were formed as couples of regioisomers depending on the location of the hydrogen abstracted. The yield increased at higher temperatures.

Attempts at cross-coupling reactions

The difference in reactivity of *tert*-butyl versus aryl sulfones led us to attempt the coupling of two different sulfones in the hope that unsymmetrical alkenes could thus be obtained.

In fact when a mixture of lithiated *tert*-butyl *n*-heptyl and phenyl *n*-pentyl sulfones (2 mmol of each) was treated with $Ni(acac)_2$ at room temperature over 3 days, a mixture of 0.7 mmol of the mixed alkene was formed by cross-coupling together with about 0.3 mmol of each of the symmetrical alkenes. This is about the statistical result.

This cross-coupling could however be of preparative value when the two starting sulfones differed greatly in chain lengths so that the more (or less) volatile compounds formed could be very readily separated. Thus methyl phenyl or ethyl phenyl sulfones were treated with *n*-dodecyl phenyl sulfone to give in low yield (25–30%), the C13 or C14 alkenes which were readily separated from the symmetrical C24 alkene. An attempt to synthesize a cyclic alkene by treatment of 1,8-bis(phenylsulfonyl) octane led to only 10% cyclooctene.

Mechanistic aspects of the homocoupling reaction

To conclude this report, some mechanistic aspects of the reaction presented above will be discussed briefly. Whereas the dimerization of stabilized carbanions promoted by a *stoichiometric* amount of oxidizing agent is a well-documented reaction, it must be pointed out that a coupling reaction between two carbanions triggered by a catalytic amount of transition metal salt is much less frequent.

Condensation of carbanions with leaving groups in the α position (sometimes called carbenoids) leading to symmetrical alkenes is well known. In the present work, the leaving group is the sulfinate anion; it is extremely poor, and indeed, sulfonyl carbanions with the usual Li, Mg or even Na and K counterions do not undergo such a coupling efficiently. The results presented above show that transition metals such as nickel catalyze this coupling reaction.

Free radical mechanism

The transition metal ions could facilitate single electron transfer. Indeed, a recent electrochemical investigation [22] has shown that a mechanism whereby a carbanion would couple with the corresponding free radical obtained after SET oxidation was possible. The dimeric radical anion thus formed would give the symmetrical alkene as well as benzenesulfinate anion and benzenesulfonyl radical. The latter could oxidize the starting carbanion and thus allow the catalytic chain to propagate. Formation of the alkene upon treatment of sulfonyl carbanions with catalytic amounts of outersphere oxidant has been reported [22].

However, in the case of nickel catalysts, bond formation (or cleavage) must take place in the coordination shell of the metal (innersphere process) as shown by the specific aspects of some catalysts, and the fact that prenyl sulfone dimerizes in the 1-1′ manner to give the triene under Ni(II) catalysis, whereas it dimerizes in the 3-3′ manner in the outersphere oxidation process [22].

Mechanism via carbenes, carbenoids and carbenic complexes

Dimerization with formation of a carbon-carbon double bond as well as cyclopropanation reaction are clearly reminiscent of a carbenic behavior. However, due to the very poor leaving group capability of the sulfonyl moiety, metallated sulfones are not prone to α-elimination. A mechanism involving free carbenes can certainly be ruled out since the stereochemical aspects of the coupling depend on the nature of the metal (lithium vs magnesium), sulfonyl group (phenyl vs *tert*-butyl) and the catalyst. Furthermore, the usual byproducts of carbene chemistry were not found.

The possibility that transmetallation changes the carbanion into an electrophilic carbenoid $PhSO_2CH(R)NiL_n$ can be considered. Another (lithiated) sulfone would then act as a nucleophile (as in the case of a coupling with well-documented electrophilic carbenoids [32]) toward this nickel species, giving a β-nickelated sulfone prone to undergo an easy β elimination of the remaining sulfonyl group. This hypothesis of an electrophilic nickel carbenoid would also explain the cyclopropanation reaction by analogy with Simmons–Smith or related reagents. However it could be shown that the nickel/sulfone cyclopropanation system is not electrophilic [17].

The formation of a nickel(II) carbene complex can also be discussed. It would be analogous to the complex formed from alkyl cyclopentadienyl nickel bearing a sulfonium group in the α position [23a].

$$L_nNiCH(R)SO_2Ph \longrightarrow L_nNi{=}CHR^+ + PhSO_2^-$$

Some investigations about the properties of α-sulfonylalkyl cyclopentadienyl nickel complexes [23b] did not bring any evidence concerning the possible formation of such a carbenic complex. Moreover, such a complex would be expected to be still more electrophilic than the corresponding carbenoid (see above).

Nickel (0) carbene complexes have also been considered recently [23c]. A few experiments [23d] have been carried out with prior reduction of the nickel salt with butyllithium. A reasonable yield of alkene was obtained showing that reduced nickel species can bring about the reaction. However the difference of reactivity between phenyl and *tert*-butyl sulfones would be difficult to understand if the active species did not bear the sulfonyl group. A similar difference has been found with the cyclopropane-forming reaction [17].

Organometallic mechanisms

A reasonable mechanistic hypothesis involves a transmetallation reaction leading to a bis α-(phenylsulfonyl) alkyl nickel(II) such as $L_nNi(CHRSO_2Ph)_2$ followed by a reductive elimination. The ensuing β-disulfone could be expected to be reduced by the nickel(0) thus formed, in a way similar to the reduction of 1,2-dibromoalkanes by zinc. This would regenerate a nickel(II) catalyst and yield the dimeric alkene. Complementary experiments were undertaken to check this hypothesis. Treatment of lithiated sulfones with a stoichiometric amount of $Ni(acac)_2$ did not give the dimeric disulfones. Stronger oxidants such as copper(II) salts appear necessary [33]. Moreover, β-disulfones are not reduced by activated nickel [24] or usual nickel zero complexes. These negative results cannot be considered as definitive evidence against the mechanism discussed here, since the stoichiometric test experiments do not perfectly reproduce the conditions of the coupling reactions (ligands on the nickel species, absence of reducer and base when working without an excess of lithiated sulfone or organometallics, etc). However the results do not favor this hypothesis, nor does the fact that such a mechanism cannot easily be 'adapted' to the formation of cyclopropanes.

The last reaction scheme to be considered involves the formation of nickelates, ie, negatively charged derivatives of nickel. Such ate complexes of nickel(II) have been shown to be powerful reagents in substitution reactions of organic halides [25]. A mechanism involving ate complexes of iron(II) has recently been proposed [26] for the related homocoupling of sulfonyl carbanions under iron catalysis.

On the other hand, ate complexes of nickel(0) have also been obtained [27] upon addition of hydride or carbanions to poorly ligated neutral nickel(0). In our case the initial nickel(II) can easily be reduced to nickel(0) by the organometallic used to deprotonate the sulfone. Addition of one or two lithiated sulfones would lead to the reactive nickelates [28].

Finally, negatively charged nickel intermediates could also easily explain the cyclopropanation activity, and especially its non-electrophilic behaviour [17].

Experimental section

^1H NMR spectra were recorded on a Cameca 250 or on a Bruker AM 400 (occasionally on a Bruker WH 80) spectrometer. The chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) or referenced to residual chloroform (7.27 ppm). Coupling constants (J) are given in hertz (Hz). Multiplicities are recorded as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). ^{13}C NMR spectra were recorded on a Cameca 250 spectrometer, ^{13}C multiplicity analyzed spectra are indicated by s (singlet, -C), d (doublet, -CH), t (triplet, $-CH_2$), q (quartet, $-CH_3$). When J-mod method spectra were used on a Bruker AM 400 at 100.57 MHz, $-CH_3$ and -CH are indicated by +; $-CH_2$ and -C are indicated as –.

Mass spectra were recorded on a Nermag R10-10B spectrometer. The following abbreviations are used: DCI, NH_3 for ammonia desorption chemical ionization and EI for electron impact.

GLC-MS using the same mass spectrometer as above and a capillary column (CPSIL-5 CB, 50 m × 0.32 mm). High resolution mass spectra were recorded on a AEI-Kratos SM 50 instrument at the Organic Spectroscopy Centre, Université Pierre-et-Marie-Curie. Melting points were determined on a Buchi 510 capillary apparatus and uncorrected.

Microanalyses were performed by the analytical laboratory of Université Pierre-et-Marie-Curie. Analytical GLC was performed on a Girdel 30 gas chromatograph using a (non-polar) capillary column.

The phenyl sulfones were obtained by condensation of allyl halides with a stoichiometric amount of sodium benzenesulfinate in DMF. Most of the phenyl sulfones used are known compounds.

Phenyl methyl mp 87 °C [29]; ethyl mp 40–42 °C [29]; propyl mp 44 °C [30]; *n*-pentyl **8**, mp 31.5 °C [31a]; *n*-heptyl

7, mp 41 °C [31b]; *n*-undecyl, mp 39 °C [32a]; *n*-dodecyl **9**, mp 36 °C [33]; benzyl **6**, mp 148 °C [34]; prenyl **3**, mp 54 °C [34]; geranyl (*p*-tolyl) **4**, mp 46 °C [34, 35]; neryl (*p*-tolyl) **4'**, mp 15–16 °C [34, 35]; geranylgeranyl **5**, oil [36]; methylthiomethyl **13**, mp 37 °C [20a]; 4-(phenylsulfonyl)butan-2-one ethylene ketal **11**, mp 40 °C [37]; 4-(phenylsulfonyl)butanoic acid **12**, mp 93 °C [38].

• *1-Methylheptyl phenyl sulfone*

Obtained from 2-bromooctane; recrystallization from pentane afforded white crystals mp 26–27 °C, 70% [39].

^{1}H NMR ($CDCl_3$, 250 MHz) 0.88 (t, J = 6.9 Hz, 3H); 1.18–1.38 (m, 8H); 1.28 (d, J = 6.9 Hz, 3H); 1.38–1.50 (m, 1H); 1.82–2.02 (m, 1H), 3.02 (m, 1H); 7.5–7.88 (m, 5H).

^{13}C NMR ($CDCl_3$, 62 MHz) 13.1 (CH_3); 14.0 (CH_3); 22.5; 26.4; 28.9; 29.0; 31.4 ($5CH_2$); 60.1 (CH); 129.0; 129.2; 133.5; 137.3 (4C arom).

MS (DCI, NH_3): m/z 254 (M^+).

Anal calc for $C_{14}H_{22}O_2S$: C, 66.08; H, 8.72. Found: C, 66.25; H, 8.87.

• *1,8-Bis(phenylsulfonyl)octane*

Mp 123 °C (dichloromethane/pentane).

^{1}H NMR ($CDCl_3$, 250 MHz) 1.11–1.45 (m, 8H); 1.55–1.80 (m, 4H); 3.08 (m, 4H); 7.5–7.7 (m, 6H); 7.85–7.95 (m, 4H).

MS (NH_3 DCI): 412 (M^+ + 18) 395 (M^+ + 1) 306, 288.

Anal calc for $C_{20}H_{26}O_4S_2$: C, 60.86; H, 6.65. Found: C, 61.02; H, 6.80.

• *1-(Methylthio)nonyl phenyl sulfone* **14**

A procedure similar to Ogura's [20b] was followed. To a mixture of (methylthio)methyl sulfone **13** [20a] (612 g, 30 mmol), sodium hydroxide (30 g) and water (30 g) at 0 °C was added a solution of bromooctane (8.7 g, 45 mmol), tetrahexylammonium bromide (0.26 g, 0.6 mmol) in toluene (50 mL). The resulting mixture was then stirred vigorously at 60 °C for 21 h. The organic layer was separated, and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with 1 M aqueous hydrochloric acid water, until pH 7, dried over magnesium sulfate and concentrated in vacuo. Recrystallization in pentane afforded white crystals mp 58 °C, 85%.

^{1}H NMR ($CDCl_3$, 250 MHz) 0.88 (t, J = 6.5 Hz, 3H); 1.20–1.35 (m, 12H); 1.45–1.55 (m, 1H); 2.10–2.22 (m, 1H); 2.22 (s, 3H); 3.68 (dd, J = 10.9 Hz, 3.1 Hz, 1H); 7.6–7.95 (m, 5H).

MS (DCI, NH_3): m/z 332 (M^+ + 18), 173.

Anal calc for $C_{16}H_{26}O_2S_2$: C, 61.10; H, 8.33. Found: C, 61.29; H, 8.43.

• *4-*tert*-Butoxybutyl phenyl sulfone* **10** *[40]*

4-Hydroxybutyl phenyl sulfone (1.0 g, 5 mmol) was treated with *tert*-butyl methyl phenyl sulfonium tetrafluoroborate (4.0 g, 15 mmol) in dichloromethane at room temperature, in the presence of potassium carbonate (2.0 g, 15 mmol) over 2 days. The yield of chromatographed product was 1.07 g (75%).

^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.12 (s, 9H); 1.45–1.83 (m, 4H); 3.12 (m, 3H); 3.30 (t, J = 6 Hz, 2H); 7.45–7.60 (m, 3H); 7.73–7.92 (m, 2H).

MS (DCI, NH_3) 288 (M^+ + 18), 271 (M^+ + 1), 232, 215 (100%), 197.

Anal calc for $C_{14}H_{22}O_3S$: C, 62.22; H, 8.15. Found C, 62.49; H, 8.30.

General procedures for the preparation of tert*-butyl sulfones*

Most of the *tert*-butyl alkyl sulfides are known compounds [41]. They were prepared by alkylation of sodium *t*-butyl thiolate with various halides according to a general procedure [42a]. To a 2 L flask containing a solution of sodium hydroxide (33.6 g, 0.84 mol) in water (570 mL) at 0 °C were added 2-methylpropane-2-thiol (56.5 mL, 0.5 mol), hexane (450 mL), alkyl bromide (0.5 mol) and tetrahexylammonium bromide (1.1 g, 2.5 mmol). After stirring vigorously at room temperature for 24 h, the reaction was stopped and the organic layer was separated from the aqueous phase which was then extracted with hexane or pentane. The combined organic layers were washed with water (2 × 150 mL) and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, leaving a clear colorless oil (90–95%) which was used in the next step without further purification in most cases.

• tert*-Butyl heptyl sulfide*

^{1}H NMR ($CDCl_3$, 250 MHz) 0.90 (t, J = 6.9 Hz, 3H); 1.22–1.40 (m, 8H); 1.36 (s, 9H); 1.50–1.62 (m, 2H); 2.5 (t, J = 7.5 Hz, 2H).

MS (CI, NH_3): m/z 188 (M^+).

• tert*-Butyl 1-methylhexyl sulfide*

^{1}H NMR ($CDCl_3$, 250 MHz) 0.89 (t, J = 6.0 Hz, 3H); 1.22–1.40 (m, 6H); 1.3 (d, J = 7.0 Hz, 3H); 1.4 (s, 9H); 1.45–1.75 (m, 2H); 2.7 (m 1H).

MS (CI, NH_3): m/z 188 (M^+).

The *tert*-butyl sulfones were prepared by oxidation of the sulfides.

• *Oxidation of the sulfides with hydrogen peroxide [42b]*

To a solution of *tert*-butyl alkyl or benzyl sulfide (0.4 mol) in acetic acid (400 mL) at 0 °C was slowly added an aqueous solution of hydrogen peroxide (110 vol, 9.8 M, 164 mL, 1.6 mol). After stirring at 80 °C for 8–16 h, the mixture was cooled to room temperature, poured into ice-water (500 mL) and extracted with ether or dichloromethane (3 × 250 mL). The combined organic layers were washed with water, saturated sodium hydrogencarbonate solution and water until pH 7, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo giving a white powder or a clear colorless oil. Recrystallization from pentane or pentane/dichloromethane or ether afforded white crystals (yield 70–80%).

• *Oxidation of the corresponding sulfide with sodium perborate*

A procedure similar to McKillop's was followed [42c]. To a 500 mL flask charged with a solution of alkyl sulfide (30 mmol) and acetic acid (60 mL) was added sodium perborate tetrahydrate (20.8 g, 120 mmol). The mixture was then stirred at 50–55 °C for 3–5 h. The reaction was complete when colorless crystalline sodium borate precipitated out; it was then cooled to room temperature and poured into water (500 mL). After extraction with dichloromethane (3 × 250 mL), the combined organic layers were washed with water, saturated sodium hydrogen carbonate, water until pH 7, and dried over magnesium sulfate. The solvent was removed in vacuo, leaving a white powder. Recrystallization from pentane or pentane/dichloromethane afforded white crystals.

• tert-*Butyl pentyl sulfone* **8a**

Mp 42 °C.

^{1}H NMR ($CDCl_3$, 250 MHz) 0.92 (t J = 7.0 Hz, 3H); 1.30–1.50 (m, 4H); 1.42 (s, 9H); 1.90 (m, 2H); 2.91 (m, 2H).

^{13}C NMR ($CDCl_3$, 62 MHz) 13.8 (CH_3); 20.3 (CH_2); 22.3 (CH_2); 23.52 ($3CH_3$); 31.0 (CH_2); 45.6 (CH_2); 58.9 (C).

MS (DCI, NH_3): m/z 210 (M^+ + 18), 193 (M^+ + 1), 154, 137.

Anal calc for $C_9H_{20}O_2S$: C, 56.19; H, 10.45. Found: C, 56.49; H, 10.49.

• tert-*Butyl heptyl sulfone* **7a**

Mp 22 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) 0.90 (t J = 7.0 Hz, 3H); 1.25–1.45 (m, 8H); 1.42 (s, 9H); 1.91 (m, 2H); 2.89 (m, 2H).

^{13}C NMR ($CDCl_3$, 62 MHz) 13.7 (q, CH_3); 20.3 (t, CH_2); 22.2 (t, CH_2); 23.17 (q, $3CH_3$); 28.5 (t, CH_2); 28.6 (t, CH_2); 31.2 (t, CH_2); 45.3 (t, CH_2); 58.9 (s, C).

MS (DCI, NH_3): m/z 238 (M^+ + 18).

Anal calc for $C_{11}H_{24}O_2S$: C, 59.95; H, 10.98. Found: C, 60.02; H, 10.92.

• tert-*Butyl dodecyl sulfone* **9a**

Mp 48.5 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) 0.90 (t J = 7.0 Hz, 3H); 1.20–1.42 (m, 18H); 1.42 (s, 9H); 1.90 (m, 2H); 2.90 (m, 2H).

^{13}C NMR ($CDCl_3$, 62 MHz) 13.9 (q, CH_3); 20.2 (t, CH_2); 22.4 (t, CH_2); 23.2 (q, $3CH_3$); 28.6–29.5 ($5CH_2$); 31.6 (t, CH_2); 45.9 (t, CH_2); 58.5 (s, C).

MS (DCI, NH_3): m/z 308 (M^+ + 18).

Anal calc for $C_{16}H_{34}OS_2$: C, 66.13; H, 11.80. Found: C, 66.25; H, 11.27.

• tert-*Butyl 1-methylhexyl sulfone*

^{1}H NMR ($CDCl_3$, 250 MHz) 0.90 (t J = 6.0 Hz, 3H); 1.20–1.40 (m, 6H); 1.40 (d, J = 7.0 Hz, 3H); 1.42 (s, 9H); 1.52 (m, 1H); 2.0 (m, 1H); 3.24 (m, 1H).

MS (DCI, NH_3): m/z 238 (M^+ + 18), 221 (M^+ + 1).

• tert-*Butyl 1-hexylheptyl sulfone*

To a 100 mL flask containing t-butyl heptyl sulfone **7a** (3.817 g, 17.4 mmol) under an argon atmosphere was added freshly distilled THF (35 mL). The solution was cooled to −78 °C (dry ice/acetone). n-Butyl lithium (11.0 mL of 1.57 M in hexane, 1.74 mmol) was then added. The mixture was stirred and allowed to reach 0 °C in 30 min. This solution of lithiated sulfone was again cooled to −25 °C and 1-iodohexane (2.70 mL, 18 mmol) was introduced. After stirring at −25 °C for 48 h the reaction was quenched by addition of saturated aqueous ammonium chloride (10 mL). After extraction with dichloromethane (3 × 50 mL) the combined organic layers were washed with water (2 × 50 mL) and dried over magnesium sulfate. The solvent was removed in vacuo leaving a white powder. Recrystallization in pentane afforded white crystals mp 53 °C, 4.7 g (90%).

^{1}H NMR ($CDCl_3$, 250 MHz) 0.89 (t, J = 6.5 Hz, 6H); 1.22–1.42 (m, 16H); 1.4 (s, 9H); 1.62–1.8 (m, 2H); 1.8–2.0 (m, 2H); 3.08 (m, 1H).

^{13}C NMR ($CDCl_3$, 62 MHz) 13.76 ($2CH_3$); 22.30 ($2CH_2$); 23.75 ($3CH_3$); 26.54 ($2CH_2$); 28.54 ($2CH_2$); 29.02 (CH_2); 31.28 ($2CH_2$); 57.16 (CH); 60.50 (C).

MS (NH_3, DCI) 322 (M^+ + 18).

Anal calc for $C_{17}H_{36}O_2S$: C, 66.83; H, 11.64. Found: C, 67.03; H, 11.92.

• tert-*Butyl 1-butylheptyl sulfone*

Prepared as the preceding sulfone except that sulfone **8a** was alkylated instead of **7a**.

Mp 49.5 °C (pentane) (85%)

^{1}H NMR ($CDCl_3$, 250 MHz) 0.8–1.0 (m, 6H); 1.2–1.5 (m, 12H); 1.42 (s, 9H); 1.63–1.80 (m, 2H); 1.8–2.0 (m, 2H); 3.09 (m, 1H).

^{13}C NMR ($CDCl_3$, 62 MHz) 13.8 (q, CH_3); 14.0 (q, CH_3); 22.5 (t, CH_2); 22.6 (t, CH_2); 24.0 (q, $C(CH_3)_3$); 26.7; 28.5; 28.7; 28.9; 29.2; 31.5 ($6CH_2$); 57.3 (CH); 60.68 (s, C).

MS (DCI, NH_3): m/z 294 (M^+ + 18), 277 (M^+ + 1), 238.

Anal calc for $C_{15}H_{32}O_2S$: C, 65.14; H, 11.67. Found: C, 65.45; H, 11.68.

General procedure for the homocoupling of metallated phenyl sulfones

The sulfone (5 mmol) was dissolved in THF (9 mL) under nitrogen in a 50 mL flask equiped with a condenser. After cooling at −78 °C the organometallic derivative (Mg or Li 5 mmol) was added and the mixture was allowed to warm up. After 1 h stirring at rt Ni(II) acetylacetonate (25.9 mg, 0.1 mmol) was added. After 15 h at rt the mixture was refluxed for 6 h and allowed to stand at room temperature. After cooling, a saturated NH_4Cl solution was added and the mixture extracted with pentane. The products were isolated by chromatography on a column of silica gel.

General procedure for the homocoupling of metallated tert-*butyl sulfones*

• *Method A: The base was added to the mixture of catalyst and sulfone*

To a light green solution of sulfone (2 mmol) and nickel acetylacetonate (10.3 mg, 0.04 mmol) in anhydrous THF (5 mL) under argon atmosphere at 0 °C was added dropwise n-butyllithium (1.27 mL of 1.61 M in hexane, 2.04 mmol). The mixture was then stirred at 25–30 °C for 15–20 h. The mixture was quenched by addition of saturated aqueous ammonium chloride (10 mL), extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with water (15 mL), dried over magnesium sulfate, and concentrated in vacuo. Purification by flash chromatography afforded the alkene as a clear colorless oil (silica gel/pentane) 80–90%; recovered sulfone (silica gel, CH_2Cl_2/AcOEt) 5–10%.

• *Method B: The catalyst was added to the preformed α-lithiated sulfone*

To a 50 mL flask equipped with condenser, containing the sulfone (2.0 mmol) under an argon atmosphere, was introduced freshly distilled anhydrous THF (5 mL). The resulting solution was cooled to 0 °C, n-butyllithium (1.24 mL of 1.61 M in hexane, 2.0 mmol) was then added dropwise via a syringe while stirring. The mixture was allowed to reach room temperature in 10–20 min. To this solution of lithiated sulfone, was introduced a preformed solution of nickel(II) acetylacetonate (Merck, 98%, water 0.5%), dried under reduced pressure (10.3 mg, 0.04 mmol) in anhydrous THF (1 mL) under an argon atmosphere. The mixture was then stirred at 25 °C for 15–20 h. During this period, the color of the reaction mixture slowly turned from pale yellow to deep yellow, orange, brown, and lithium sulfinate was gradually precipitated. The work-up was the same as with *Method A*.

The secondary alkyl *tert*-butyl sulfones were treated according to *Method A*.

• *2,7-Dimethylocta-2,4,6-triene* **21**

From the magnesium derivative of phenyl prenyl sulfone **3**.

UV (isooctane) λ_{max} at 270, 279.5, 291 nm in agreement with the literature [43].

• *2,6,11,15-Tetramethylhexadeca-2,6,8,10,14-pentaene (*EZE *and* EEE*)* **22**

From the magnesium derivative of *p*-tolyl geranyl sulfone **4**.

UV (isooctane) λ_{max} at 275, 285, 297.4 nm in agreement with the literature [11b].

^{1}H NMR (250 MHz) 1.62 (br s, 6H); 1.70 (s, 6H); 1.78 (s, 6H); 2.06–2.16 (m, 8H); 5.12 (m, 2H); 5.88; 6.16; 6.36 (m, 4H).

^{13}C NMR 16.67; 16.93; 17.90; 25.86; 26.89; 40.23; 40.55; 120.11; 123.15; 123.86; 125.22; 127.04; 131.37; 137.78; 139.08 in agreement with the literature [12a].

• *2,6,11,15-Tetramethylhexadeca-2,6,8,10,14-pentaene (*ZEZ *and* ZZZ*)* **22′**

From the magnesium derivative of *p*-tolyl neryl sulfone **4′**.

UV (isooctane) λ_{max} at 274.2, 285, 297.7 nm in agreement with the literature [11b].

^{1}H NMR (250 MHz) 1.61 (br s, 6H); 1.69 (s, 6H); 1.80 and 1.85 (2s, 6H); 1.96–2.24 (m, 8H); 5.12 (m, 2H); 5.75–6.19 (m, 4H).

^{13}C NMR 17.83; 24.11; 24.50; 25.86; 27.09; 32.46; 32.79; 120.82; 122.70; 123.93; 126.06; 126.65; 131.50; 137.98; 139.21 in agreement with the literature [12a].

• *Phytoene; 7,7′,8,8′,11,11′,12,12′-octahydro-ψ,ψ′-carotene* **23**

From the magnesium derivative of geranylgeranyl phenyl sulfone.

UV (isooctane) λ_{max} at 275.5, 286, 298.5 nm in agreement with the literature [11b].

^{1}H NMR (250 MHz) 1.60 (s, 12H); 1.62 (s, 6H); 1.68 (s, 6H); 1.78 (s, 6H); 1.93–2.20 (m, 24H); 5.13 (m, 6H); 5.94–6.14 (m, 2H); 6.36 (m, 2H).

^{13}C NMR 16.22; 16.67; 16.93; 17.83; 25.86; 26.83; 26.96; 39.52; 39.84; 40.23; 40.62; 120.17; 123.15; 123.80; 124.05; 124.25; 125.35; 127.04; 130.92; 134.99; 137.65; 139.01 in agreement with the literature [44].

• *Dec-5-ene (*E + Z*) and tetradec-7-ene* E + Z

Prepared from pentyl sulfone (**8** or **8a**) and heptyl sulfone (**7** or **7a**) respectively. The spectra were in agreement with those of the commercial products (Aldrich).

• *Tetracos-12-ene* E + Z

Prepared from *tert*-butyl dodecyl sulfone **9a** or dodecyl phenyl sulfone **9**.

^{1}H NMR ($CDCl_3$, 250 MHz) 0.9 (t, J = 6.9 Hz, 6H); 1.20–1.35 (m, 36H); 1.90–2.05 (m, 4H); 5.30–5.45 (m, 2H).

^{13}C NMR ($CDCl_3$) 14.0 (CH_3); 22.6; 27.1; 29.1; 29.2; 29.3; 29.5; 29.6; 30.1; 31.9; 32.5 (CH_2); 129.7; 130.2 (CH).

MS (EI): m/z 336 (M^+), 153, 125, 111, 97, 83, 69, 55 (100), 53.

Anal calc for $C_{24}H_{48}$: C, 85.62; H,14.38. Found: C, 85.46; H, 14.51.

• *7,8-Dimethyltetradec-7-ene* E + Z

Prepared from 1-methylheptyl phenyl sulfone and identified only by MS (224, M^+).

• *7,8-Dibutyltetradec-7-ene* E + Z

Prepared from *tert*-butyl 1-butylheptyl sulfone.

^{1}H NMR ($CDCl_3$, 250 MHz) 0.92 (m, 12H); 1.25–1.35 (m, 26H); 1.92–2.05 (m, 8H).

^{13}C NMR ($CDCl_3$) 14.1 (CH_3); 22.7; 22.9; 23.1; 29.2; 29.3; 29.7; 29.9; 31.3; 31.5; 31.6 (CH_2); 133.4 (C).

MS (EI): m/z 308 (M^+), 224, 182, 154, 111, 97, 83, 69, 55 (100), 53.

HDRMS for $C_{22}H_{44}$: Calc, 308.3443; Found: 308.3446.

• *7,8-Dihexyltetradec-7-ene*

Prepared from *tert*-butyl 1-hexylheptyl sulfone.

^{1}H NMR ($CDCl_3$, 250 MHz) 0.90 (t, J = 6.5 Hz, 12H); 1.2–1.4 (m, 32H); 1.92 (t, J = 8 Hz, 8H).

^{13}C NMR ($CDCl_3$) 14.0 (CH_3); 22.6; 29.1; 29.5; 31.4; 31.7 (CH_2); 133.3 (C).

MS (EI): 364 (M^+), 280, 210, 182, 125, 111, 97, 83, 69, 55 (100).

Anal calc for $C_{26}H_{52}$: C, 85.63; H,14.37. Found: C, 85.24; H, 13.99.

• *1,2-Bis(methylthio)ethene* (E + Z)

Prepared from (methylthio)methyl phenyl sulfone **13**.

^{1}H NMR ($CDCl_3$, 250 MHz) 2.26 and 2.36 (2s, 6H, (*E*)-CH_3, (*Z*)-CH_3); 6.0 and 6.1 (2s, 2H, (*Z*)-CH, (*E*)-CH) in agreement with the literature [45].

MS (EI): 120 (M^+), 105 ($M^+ - CH_3$), 88, 71, 61 (100), 58.

• *Oct-4-ene-2,7-dione bis ethyleneketal*

Obtained from sulfone **11** as a mixture of *E* and *Z* isomers.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.31 (s, 3H); 1.34 (s, 3H); 2.38 (m, 2H); 2.44 (m, 2H); 3.98 (s, 8H); 5.58 (m, 1H); 5.65 (m, 1H).

• *Tridec-1-ene*

Prepared from the cross-coupling reaction of dodecyl phenyl sulfone and methyl phenyl sulfone. Tridec-2-ene was prepared from the cross-coupling reaction of ethyl phenyl sulfone and phenyl undecyl sulfone.

• *Reaction of phenyl prenyl sulfone* **3** *with potassium hydride (0.5 equiv)*

A suspension of KH (330 mg, 0.75 mmol) in THF (2 mL) was prepared under nitrogen. A solution of sulfone **3** (315 mg, 1.5 mmol) in THF (3 mL) was added, leading to an orange solution. The reaction mixture was stirred for 18 h at room temperature, hydrolyzed with a saturated aqueous solution of ammonium chloride and extracted with ether. The crude extract (230 mg) was chromatographed, leading to the cyclopropylic sulfone **17** (45.7 mg, 22%) and the disulfone **16** (84 mg, 27%) as a mixture of diastereomers.

• *1-(Phenylsulfonyl)-2-isobutenyl-3-isopropyl-cyclopropane* **17**

^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.73 (d, J = 6.5 Hz, 3H); 0.92 (d, J = 6.5 Hz, 3H); 1.15–1.32 (m, 1H); 1.53 (td, J = 10 Hz, J = 5 Hz, 1H); 1.70 (s, 3H); 1.72 (s, 3H); 2.15 (t, J = 5 Hz, 1H); 2.59 (td, J = 9.5 Hz, J = 5 Hz, 1H); 4.84 (d, J = 9.5 Hz, 1H); 7.50–8.0 (m, 5H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ 18.3 (CH_3); 21.3 (CH_3); 22.1 (CH_3); 23.9 (CH); 25.7 (CH_3); 27.3 (CH); 33.5 (CH); 46.1 (CH); 117.2; 127.1; 128.7; 132.8; 136.9; 140.4.

These spectra are in very good agreement with the *p*-tolyl analogs described previously [15b], and correspond to one isomer displaying the sulfonyl group in *trans* position to both alkyl groups.

MS (EI) m/z 228.

• *4-Phenylsulfonyl-5-[(phenylsulfonyl)methyl]-2,6-dimethylhept-2-ene* **16**

First isomer mp 151 °C (ether).

^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.58 (d, J = 7 Hz, 3H); 0.78 (d, J = 7 Hz, 3H); 1.18 (s, 3H); 1.72 (s, 3H); 2.58 (hept, J = 7 Hz, 1H); 2.76–3.06 (m, 3H); 4.67 (dd, J = 11.5 Hz, J = 2 Hz, 1H); 5.37 (d, J = 11.5 Hz, 1H); 7.54–8.0 (m, 10H).

MS (DCI, NH_3) m/z 421 (M^+ + 1).

Second isomer mp 122 °C (ether).

^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.75 (d, J = 7 Hz, 3H); 0.86 (d, J = 7 Hz, 3H); 1.18 (s, 3H); 1.68 (br s, 3H); 2.54 (hept t, J = 7 Hz, J = 3.5 Hz, 1H); 2.86 (br d, J = 10.5 Hz, 1H); 3.27 (dd, J = 14 Hz, J = 10.5 Hz, 1H); 3.90 (dd, J = 11.5 Hz, J = 1.5 Hz, 1H); 3.98 (dd, J = 14 Hz, J = 3 Hz, 1H); 5.10 (d, J = 11.5 Hz, 1H); 7.54–8.0 (m, 10H).

MS (DCI, NH_3) m/z 421 (M^+ + 1).

The same reaction with potassium *tert*-butoxide (1 equiv) instead of potassium hydride (0.5 equiv) gave the triene **20** (20%), the cyclopropylic sulfone **17** (26%) and the dienyl sulfone **18** (26%).

• *2,6-Dimethyl-5-methylenehepta-1,3-diene* **20**

UV (petroleum ether) λ_{max} 250.4, 260.0, 270.9 nm.

^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.15 (d, J = 7 Hz, 6H); 1.90 (br s, 3H); 2.65 (hept, J = 7 Hz, 1H); 5.07 (m, 4H); 6.18 (d, J = 17 Hz, 1H); 6.48 (d, J = 17 Hz, 1H).

• *5-[(Phenylsulfonyl)methyl]-2,6-dimethylhepta-1,3-diene* **18**

Mp 39 °C (pentane).

^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.82 (d, J = 7 Hz, 3H); 0.86 (d, J = 7 Hz, 3H); 1.59 (s, 3H); 1.70–1.89 (m, 1H); 2.51–2.65 (m, 1H); 3.24 (d, J = 4.5 Hz, 1H); 3.27 (d, J = 1.5 Hz, 1H); 4.89 (s, 1H); 4.92 (s, 1H); 5.14 (dd, J = 16 Hz, J = 9.5 Hz, 1H); 6.01 (d, J = 16 Hz, 1H); 7.50–7.92 (m, 5H).

• *Preparation of an authentic sample of 6-[(phenylsulfonyl)methyl]tridecane* **19** *(R = pentyl)*

Condensation of lithiated methyl phenyl sulfone with hexanal and quenching with acetic anhydride gave 1-phenylsulfonyl-2-acetoxyheptane in 95% yield.

^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.85 (m, 3H); 1.1–1.5 (m, 6H); 1.5–1.75 (m, 2H); 1.80 (s, 3H); 3.2–3.6 (m, 2H); 5.12–5.65 (m, 1H); 7.5–8.10 (m, 5H).

MS (EI), m/z: 298.

To a solution of the crude acetate (2.90 g, 10 mmol) in dioxane (36 mL) under nitrogen was added powdered sodium hydroxide (600 mg, 15 mmol) and the mixture was vigorously shaken at 20 °C for 8 h. After hydrolysis and ether extraction, phenyl hept-1-enyl sulfone (E isomer) was obtained (2.15 g, 90% pure).

^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.87 (m, 3H); 1.1–1.75 (m, 6H); 2.05–2.40 (m, 2H); 6.35 (d, J = 15 Hz, 1H); 7.02 (d, J = 15 Hz, t, J = 7 Hz, 1H); 7.5–8.1 (m, 5H).

MS (EI), m/z: 238.

This vinyl sulfone (1.19 g, 5 mmol) was dissolved in THF (10 mL) and cuprous bromide (36 mg, 0.25 mmol) was added. After cooling to 0 °C a solution of n-heptylmagnesium chloride (10 mmol) in THF (10 mL) was added. After 2 h stirring at rt, hydrolysis and ether extraction, the crude product (1.6 g) was chromatographed (pentane/ethyl acetate). Sulfone **19** (650 mg, 38%) was thus obtained.

^{1}H NMR (250 MHz, $CDCl_3$) δ 0.80–0.94 (m, 6H); 1.08–1.48 (m, 20H); 1.96 (hept, J = 6 Hz, 1H); 3.05 (d, J = 6 Hz, 2H); 7.54–7.74 (m, 3H); 7.90–8.0 (m, 2H).

^{13}C NMR ($CDCl_3$) 14.1; 14.2; 22.6; 22.7; 25.7; 26.0; 29.0; 29.6; 31.9; 33.1; 33.2; 60.2; 127.7; 128.6; 133.1; 139.9.

MS (EI), m/z: 339 (M^+ + 1), 321, 267, 239, 143.

• *1-(Phenylsulfonyl)-2-methylpentane* **19** *(R = Me)*

Isolated in 13% yield in the coupling of phenyl propyl sulfone.

^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.75–0.92 (m, 3H); 1.06 (d, J = 7 Hz, 3H); 1.12–1.44 (m, 4H); 1.82–2.30 (m, 1H); 2.77–3.26 (m, 2H); 7.5–8.1 (m, 5H).

^{13}C NMR ($CDCl_3$) 14.1; 19.7; 20.0; 28.5; 39.0; 62.6; 127.6; 129.0; 133.2; 140.0.

MS (EI), m/z: 226 (M^+ + 1), 209, 143 ($PhSO_2H_2$), 125, 119, 105, 85 (M^+ – $PhSO_2$), 77.

• *7,8-Bis(phenylsulfonyl)tetradecane*

This was prepared by oxidative dimerization of heptyl phenyl sulfone **7** [33, 46].

To a solution of sulfone **7** (430 mg, 1.8 mmol) in THF (2 mL) at −50 °C was added n-butyllithium (1.6 M solution in hexane, 2 mmol) followed by cupric triflate (790 mg, 2.2 mmol) in isobutyronitrile (2.2 mL). After 1 h at −50 °C the mixture was stirred at room temperature for 18 h, hydrolyzed with saturated aqueous ammonium chloride and extracted with methylene chloride. Flash chromatography gave the diastereomers.

• meso *isomer (84 mg, 20%) mp 90 °C (CH_2Cl_2/pentan*

^{1}H NMR (80 MHz, $CDCl_3$) 0.85 (m, 6H); 1.05–1.24 (m, 16H); 1.92 (m, 4H); 3.72 (t, J = 6 Hz, 2H); 7.5–7.9 (m, 10H).

MS (EI), m/z: 478 (M^+ + 1) weak, 337, 195, 143, 125, 111, 97, 77, 69, 53.

Anal calc for $C_{26}H_{38}O_4S_2$: C, 65.25; H, 8.00. Found: C, 64.94; H, 8.22.

• dl *isomer (84 mg 20%), mp 139 °C (CH_2Cl_2/pentane)*

^{1}H NMR (80 MHz, $CDCl_3$) 0.85 (m, 6H); 1.05–1.23 (m, 16H); 2.02 (m, 4H); 3.78 (t, J = 6 Hz, 2H); 7.55–8.0 (m, 10H).

MS (EI), m/z: 478 (M^+ + 1) weak, 337, 195, 143, 127, 111, 97, 83, 77, 69.

Anal calc for $C_{26}H_{38}O_4S_2$: C, 65.25; H, 8.00. Found: C, 65.18; H, 8.09.

The configurations were assigned according to the NMR spectra and a kinetic resolution by elimination carried out with a chiral base [47].

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References and notes

1 a) Tanaka K, Kaji A, *Synthetic Uses of Sulfones*, in *The Chemistry of Sulfones and Sulfoxides*, Patai S, Rappoport Z, Stirling C Eds, Wiley, New York, 1988, chap 15 and references cited therein

b) Simpkins NS, *Sulfones in Organic Synthesis*, Pergamon, Oxford, 1993

c) Schank K, in *Houben-Weyl Methoden der Organischen Chemie*, Klamann D Ed, Thieme, Stuttgart, 1985, vol E11, p 1129
d) Brown DS, Bruno M, Davenport RJ, Ley SL, *Tetrahedron* (1989) 45, 4293

2 a) Fabre JL, Julia M, Verpeaux JN, *Bull Soc Chim Fr* (1985) 762
b) id, ibid 772

3 Posner GH, Brunelle DJ, *J Org Chem* (1973) 38, 2747

4 Kochi JK, *Organometallic Mechanisms and Catalysis*, Academic, New York, 1978

5 a) Julia M, Righini A, Verpeaux JN, *Tetrahedron Lett* (1979) 26, 2393; *Tetrahedron* (1983) 39, 3289
b) Trost BM, Schmuff NR, Miller MJ, *J Am Chem Soc* (1980) 102, 5979

6 a) Field L, *Synthesis* (1972), 101 and references cited therein
b) Truce WE, Klingler TC, *J Org Chem* (1970) 35, 1834

7 a) Matthews WS, Bares JE, Bartmess JE, Bordwell FG, Kornforth JF, Drucker GE, Margolin Z, Mc Callum RJ, Mc Callum GJ and Varrier NR, *J Am Chem Soc* (1975) 97, 7006
b) Bordwell FG, Bares JE, Bartmess JE, Mc Callum GJ, Van Der Preg M, Varrier NR and Matthews, *J Org Chem* (1977) 42, 321

8 a) Jones MA, Moss RA, *Carbene*, Wiley, New York, Vol 2, 1975
b) *Houben Weyl, Methoden der Organischen Chemie*, Regitz M Ed, Thieme, Stuttgart, 1989, Vol E19b

9 Mc Murry JE, *Acc Chem Res* (1983) 16, 405; *Chem Rev* (1989) 89, 1513

10 Julia M, Verpeaux JN, *Tetrahedron Lett* (1982) 23, 2457; see also Verpeaux JN, Thèse de doctorat d'État de l'université Paris VI (1981)

11 a) Davis JB, Jackman LM, Siddons PT, Weedon BCL, *J Chem Soc (C)* (1966) 2154
b) Khan N, Lober DE, Toube TB, Weedon BCL, *J Chem Soc, Perkin I* (1975) 1457

12 a) Barlow L, Pattenden G, *J Chem Soc, Perkin I* (1976) 1029
b) Clough JM, Pattenden G, *Tetrahedron Lett* (1978) 4159

13 a) Kocienski PJ, Lythgoe B, Waterhouse I, *J Chem Soc, Perkin I* (1980) 1045
b) Lythgoe B, Waterhouse I, *J Chem Soc, Perkin I* (1979) 2429

14 a) Julia M, Paris JM, *Tetrahedron Lett* (1973) 4833
b) Julia M, *Pure Appl Chem* (1985) 57, 763

15 a) Goodwin TW in *Carotenoids*, Isler O, Ed, Birkhäuser, Basel, 1971, p 577
b) Takikawa Y, Osanai K, Sasaki S, Shimada K, *Chem Lett* (1987) 1939

16 Mulvaney JE, Savage D, *J Org Chem* (1971) 36, 2592

17 a) Gai Y, Julia M, Verpeaux JN, *Synlett* (1991) 56; *id, ibid* 269
b) Gai Y, Julia M, Verpeaux JN, *Bull Soc Chim Fr* (1996) 133, 817

18 Engman L, *J Org Chem* (1984) 49, 3559

19 Jin L, Julia M, Verpeaux JN, *Synlett* (1994) 215

20 a) Ogura K, Yahata N, Watanabe J, *Bull Chem Soc Jpn* (1983) 56, 3543
b) Ogura K, Yahata N, Haskizume K, Tsuyam K, Takahaski K, Ida H, *Chem Lett* (1983) 767

21 Gai Y, Jin L, Julia M, Verpeaux JN, *J Chem Soc, Chem Commun* (1993) 1625

22 a) Amatore C, El Moustafid T, Rolando C, Thiébault A, Verpeaux JN, *Tetrahedron* (1991) 47, 777
b) Amatore C, Thiébault A, Verpeaux JN, *J Chem Soc, Chem Commun* (1989) 1543

23 a) Davidson JG, Barefield EK, van Derveer DG, *Organometallics* (1985) 4, 1178
b) Julia M, Lauron H, Verpeaux JN, *J Organomet Chem* (1990) 387, 365
c) Eisch JJ, Qian Y, Singh MJ, *Organomet Chem* (1996) 512, 207
d) Experiments carried out by I Daub

24 Prepared according to Riecke RD, *Acc Chem Res* (1977) 10, 301

25 Corey EJ, Posner GL, *Tetrahedron Lett* (1970) 315

26 Jin L, Julia M, Verpeaux JN, *CR Acad Sci Paris* (1994) 319, 1475

27 Jonas K, Krüger C, *Angew Chem Int Ed Engl* (1980) 19, 520; Wilke G, *Angew Chem Int Ed Engl* (1988) 27, 185; Kaschube W, Pörshke KR, Bourath W, Krüger C, Wilke G, *Angew Chem Int Ed Engl* (1989) 28, 772 and references therein

28 Such nickelates can also be seen as the reduced forms of the bis-sulfonylalkyl nickel(II) discussed in the preceding paragraph. The extra electrons would be responsible for the enhanced reactivity, a scheme which is clearly related to the electron transfer activation of organometallic processes see ref 4 and *Organometallic Radical Processes*, Trogler WC Ed, *J Organomet Chemistry Library*, Elsevier, Amsterdam, 1990

29 Fields L, Clark RD, *J Org Chem* (1957) 22, 1129

30 Baldwin WA, Robinson R, *J Chem Soc* (1932) 1445

31 a) Paris JM, Thèse de docteur-ingénieur de l'université Paris VI (1974)
b) Uguen D, Thèse de doctorat d'État de l'université Paris VI (1976)

32 a) Charreau P, Julia M, Verpeaux JN, *J Organomet Chem* (1989) 379, 201
b) Lima C de, Julia M, Verpeaux JN, *Synlett* (1992), 133

33 Baudin JB, Julia M, Rolando C, Verpeaux JN, *Tetrahedron Lett* (1984) 3203; *Bull Soc Chim Fr* (1987) 493

34 Uguen D, Julia M, *Bull Soc Chim Fr* (1976) 513

35 Terao S, Kato K, Shiraishi M, Morimoto H, *J Chem Soc, Perkin Trans I* (1978) 1101

36 Campbell RVM, Crombie L, Findley DAR, King RW, Pattenden G, *J Chem Soc, Perkin Trans I* (1975) 897

37 Julia M, Badet B, *Bull Soc Chim Fr* (1975) 1363

38 Thomson CM, Frick JA, *J Org Chem* (1989) 54, 890

39 Manesalchi F, Orena M, Savoia D, *Synthesis* (1979) 6, 445

40 Mallet JM, Thèse de doctorat de l'université Paris VI, 1988

41 Goldwhite H in *Rodd's Chemistry of Carbon Compounds*, Coffry S Ed, Elsevier, Amsterdam, 1965, IB, p 78

42 a) Herriott AW, Picker D, *Synth Commun* (1975) 477
b) Paquette LA, Carr RIC, *Org Synth* (1986) 64, 157
c) McKillop A, Tarbin JA, *Tetrahedron Lett* (1983) 1505

43 Eriksen J, Krogh-Jespersen K, Ratner MA, Schulster DI, *J Am Chem Soc* (1975) 97, 5596; Josey AD, *J Org Chem* (1974) 39, 139

44 Granger P, Maudinas B, Herber R, Villoutreix J, *J Magn Res* (1973) 10, 43

45 Tiecco M, Testaferri L, Tingoli M, Chianalli D, Montanucci M, *J Org Chem* (1983) 48, 4795

46 Julia M, Le Thuillier G, Rolando C, Saussine L, *Tetrahedron Lett* (1982) 23, 2453

47 Julia M, Lauron H, Stacino JP, Verpeaux JN, *Tetrahedron* (1986) 42, 2475

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Conversion of non-activated alkenes into cyclopropanes with lithiated sulfones under nickel catalysis

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Summary — Lithiated alkyl *tert*-butyl sulfones convert alkenes into cyclopropane derivatives under nickel catalysis. The new reaction appears to differ from the known cyclopropanation reactions from both the stereochemical and the electronic points of view.

sulfone / sulfonyl carbanion / alkene / cyclopropanation / nickel

Résumé — Cyclopropanation d'alcènes non activés par des sulfones lithiées en présence de nickel. *Les alkyl* tert*-butyl sulfones lithiées, en présence d'une quantité catalytique de nickel peuvent transformer les alcènes en cyclopropanes. Cette nouvelle réaction présente des caractéristiques différentes de celles des méthodes usuelles de cyclopropanation.*

sulfone / carbanion sulfonylé / alcène / cyclopropanation / nickel

Introduction

The use of sulfones in organic synthesis has increased considerably in recent years [1, 2]. In most cases the easy deprotonation in the α-position leads to a carbanion which undergoes reaction with electrophiles. The sulfonyl group is then removed, mainly by reduction or, more rarely, elimination. On the other hand, the allylic sulfones undergo direct substitution reactions with Grignard reagents under copper catalysis [3], with organoaluminium compounds [4a], with stabilized anions under palladium [4b] or nickel catalysis [4c].

During investigations of the Grignard reaction, the question arose as to whether other metals could catalyze the reaction. It turned out that some metallated allylic sulfones were converted into symmetrical trienes with loss of the sulfonyl group when treated with nickel(acac)$_2$ [5]; very little substitution of the sulfonyl group was observed. A side reaction was the elimination of the sulfonyl group leading to the alkene with the same number of carbon atoms as the starting sulfone [6].

Another side reaction was the formation of cyclopropane derivatives by reaction of a third molecule of metallated sulfone with either the symmetrical alkene formed in situ or an added alkene. In these early experiments, lithiated sulfones proved much better than magnesiated analogs to achieve the cyclopropanation reaction [5]. During an extensive investigation of the coupling reaction [7], this cyclopropane formation turned up again and is the object of the present report. The conditions under which it took place were very different from those of the common cyclopropane-forming reactions and appeared worth investigating. Preliminary communications have been made [8].

Optimization of the reaction

The experimental conditions had to be chosen in such a way as to maximize the desired reaction and minimize both the symmetrical coupling and the elimination. These preliminary experiments were carried out with lithiated *tert*-butyl pentyl sulfone and styrene (1 equiv of each); various experimental procedures were compared.

In *Technique A*, the base BuLi or MeLi (1 equiv) was introduced into a THF solution of the sulfone, Ni(acac)$_2$ and the alkene at 0 °C; the temperature was then raised to 20 °C. In *Technique B*, the sulfone was lithiated in THF first, and then a solution of the alkene and Ni(acac)$_2$ was added at 0 °C and the mixture allowed to warm to room temperature. In *Technique C*, the base was added to the sulfone and Ni(acac)$_2$ in THF at 0 °C, and then the alkene was introduced and the temperature raised to room temperature. In *Technique D*, the base was added to a solution of the alkene and Ni(acac)$_2$ at −78 °C, a solution of the sulfone in THF was added and the temperature was raised to room temperature. In *Technique E*, the base was very slowly added to a solution of the sulfone, the alkene and Ni(acac)$_2$ in THF at room temperature.

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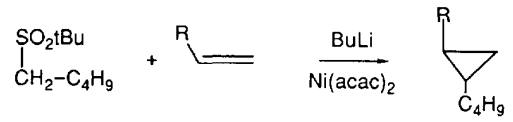
The yield of 1-phenyl-2-butylcyclopropane was respectively 20, 19, 15, 10 and 50%. Some (5–10%) of the starting sulfone was recovered, and the major by-product was dec-5-ene. Such results can be understood if it is assumed that the desired reaction is first order in the sulfonyl carbanion and the alkene, whereas the homocoupling is second order in the sulfonyl carbanion. A high yield in cyclopropane requires maintenance of the concentration of sulfonyl anions at a low level. This provides a good explanation for the higher yield obtained with *Technique E*. However, since the other techniques are more convenient, further comparison between *Technique A* and *Technique E* was carried out. For the same kinetic reasons the concentration of alkene was varied (table I).

Table I. Influence of the alkene concentration in the cyclopropanation of styrene or oct-1-ene with lithiated *tert*-butyl pentyl sulfone (2% $Ni(acac)_2$, at 20 °C, 25 h in THF).



Alkene (R)	*Equiv*	*Technique*	*Yield (%) (glc)*	trans/cis
Ph	1	A	20	60:40
Ph	20	A	54	60:40
Ph	1	E	50	61:39
Ph	20	E	80	61:39
n-C_6H_{13}	6	A	40	44:56
n-C_6H_{13}	15	E	89	45:55

It can be seen that a sizable increase in yield was observed when excess alkene was used. This has been common practice in most cyclopropane-forming reactions.

As regards the solvent (table II), a few experiments showed that with BuLi in hexane as base, increasing the proportion of hexane in the THF had a deleterious effect even when using a large excess of alkene. Diethyl ether was less efficient than THF. When MeLi in diethyl ether was used, however, the same solvent was quite satisfactory; DMSO, DMF, HMPA or acetonitrile gave practically no cyclopropane.

As regards the temperature, the reaction was definitely faster at 65 °C than at 25 °C, but the stereoselectivity decreased somewhat. The amount of symmetrical alkene formed also decreased, showing that the homocoupling was less accelerated by an increase in temperature (table III) than the cyclopropanation. In all cases, conversion of the sulfone was high (2–6% recovered).

A few nickel salts were compared (table IV) in the cyclopropanation of hex-1-ene with *tert*-butyl pentyl sulfone, using the simple *Technique A*.

With $Ni(acac)_2$, a 2% proportion appeared to be suitable; the hydrated form (Aldrich) being somewhat superior to the anhydrous salt. Perhaps the lithium hydroxide thus produced is responsible; other cases are known where alkali alkoxides have a strong influence on the behavior of organometallics [9]. The hexafluoroacetoacetonate proved less active. Nickel hydroxide, carbonate, or sulfate were inactive. Among the halides, large differences were observed with the bromide being the more efficient.

Indeed nickel bromide was even slightly better than nickel acetylacetonate in *Technique A*. However, in *Technique E*, the latter proved somewhat more efficient. All the results described above point to the superiority of *Technique E* where the base is added slowly to the reaction mixture. For this reason, insoluble bases such as lithium hydride were not tried since their slow addition through a syringe pump were not pratically feasible.

These preliminary investigations led to a preferred procedure very similar to *Technique E*: a slow addition (duration t_1) of MeLi in diethyl ether to the mixture

Table II. Influence of the solvent in the cyclopropanation of styrene (20 equiv) with *tert*-butyl pentyl sulfone, 2% $Ni(acac)_2$, room temperature, 24 h.

Base	*Solvent*			*Technique*	*Cyclopropane*		*Dec-5-ene yield (%)*	*Starting sulfone (%)*
	Hexane	*Et_2O*	*THF*		*Yield (%) (glc)*	trans/cis		
n-BuLi	2.5	0	10	A	54	60:40	5	20
n-BuLi	12	0	0.5	A	16	59:41	36	26
n-BuLi	2.5	10	0	A	30	60:40	31	20
n-BuLi	2.5	0	10	E	80	60:40		
n-MeLi	0	2.5	10	E	91	60:40		

Table III. Influence of the temperature: alkene with *tert*-butyl pentyl sulfone in THF, 2% $Ni(acac)_2$ (*Technique E*).

Alkene	*Equiv*	*t (°C)*	*Duration (h)*	*Cyclopropane (%) (glc)*	trans/cis (exo/endo)
Styrene	1.2	25	17	60	60:40
Styrene	1.2	65	3.5	91	53:47
Cyclooctene	15	25	23	50	99:1
Cyclooctene	15	40	20	59	98:2
Cyclooctene	15	65	24	70	97:3

Table IV. Comparison of nickel derivatives: *tert*-butyl pentyl sulfone, hex-1-ene (5 equiv) in THF, 25 °C, 24 h (*Technique A*).

Catalyst	*Equiv (%)*	*MeLi (equiv)*	*Cyclopropane*		*Dec-5-ene (%)*	*Starting sulfone (%)*[a]
			Yield (%)	trans/cis		
$Ni(acac)_2$	1	1.0	20	40:60	49	20
$Ni(acac)_2$	2	1.0	40	39:61	46	5
$Ni(acac)_2$	4	1.0	35	40:60	40	15
$Ni(acac)_2$[b]	4	1.05	60	41:59	20	4
$Ni(acacF_6)_2$[b,c]	4	1.05	32	40:60	34	20
NiF_2	4	1.05	4	39:61	60	21
$NiCl_2$[b]	4	1.05	26	41:59	50	10
$NiBr_2$	3	1.05	70	38:62	12	6
NiI_2[b]	4	1.0	23	43:57	40	20
$Ni(OAc)_2$[b]	2	1.1	10	40:60	57	15
$Ni(NO_3)_2 \cdot 6H_2O$	2	1.1	3	40:60	44	30

[a] GLC; [b] hydrated form of the catalyst (the percentage was calculated with one H_2O per mole); [c] acacF_6 = $CF_3COCHCOCF_3$.

containing the sulfone; a slight excess of alkene; 2% $Ni(acac)_2$ or $NiBr_2$; and reaction (duration t_2) carried out in refluxing THF. This standard technique was used in determining the scope of the reaction and is referred to as the 'standard technique' in the following.

Scope of the reaction: substitution pattern in sulfone and alkenes

With methyl sulfones: methylenation

By far the most common cyclopropanation reactions are methylenations, so the methyl sulfones were investigated first. The preliminary experiments mentioned above were carried out with *tert*-butyl sulfones following the observation that these were more reactive than the phenyl sulfones in the homocoupling reaction [7]. When three methyl sulfones were compared in the cyclopropanation of styrene or dec-1-ene (1.2 equiv) in refluxing THF (table V) notable differences appeared.

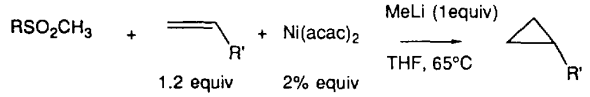
Whereas dimethyl sulfone and phenyl methyl sulfone proved mediocre with styrene and very poor with dec-1-ene, *tert*-butyl methyl sulfone converted both olefins into cyclopropanes in good yields, the aliphatic alkene being less reactive than styrene. The advantage of using *tert*-butyl sulfones was much more marked than in the homocoupling reaction. Some differences had previously been noticed between these two kinds of sulfones [7, 10].

It seems difficult to ascribe the present difference to the slight difference in pK_a between alkyl and aryl sulfones [11], since dimethyl sulfone is very similar to *tert*-butyl sulfone in this respect. The lithium *tert*-butylsulfinate formed in the reaction can be easily isolated and converted again into *tert*-butyl methyl sulfone.

When terminal alkenes were treated with *tert*-butyl methyl sulfone in a similar way the methylenation proved general (table VI). The yields ranged from 65 to 99% even with practically equimolecular amounts of sulfone and alkene; excess alkene could increase these yields.

A preparative-scale experiment (6.7 mmol) was carried out in the case of methylenation of dodec-1-ene. A 1.5 molar equivalent excess of olefin was used. The crude mixture of hydrocarbons was treated by sodium periodate in the presence of ruthenium catalyst to oxidize the remaining olefin. Simple chromatography then provided the cyclopropane as a pure (98%) product, with an isolated yield of 66%. The same procedure with

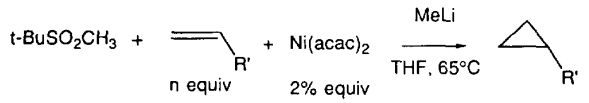
Table V. Methylenation of styrene or dec-1-ene (1.2 equiv) with lithiated methyl sulfone (standard technique).



R	*R'*	t_1 *(h)*[a]	t_2 *(h)*[b]	*GC yield (%)*
Me	Ph	2.5	0.5	15
Ph	Ph	2.5	0.5	12
t-Bu	Ph	2.5	0.5	99
Me	*n*-Oct	7	7	<5
Ph	*n*-Oct	7	11	<5
t-Bu	*n*-Oct	4.5	3.5	65

[a] Duration of the addition of MeLi; [b] refluxing time after the end of addition of MeLi.

Table VI. Methylenation of terminal alkenes with slowly generated *tert*-Bu-SO_2-CH_2Li (standard technique).



Alkene	*Equiv*	t_1 *(h)*[a]	t_2 *(h)*[b]	*Yield (%) GLC (isolated)*
Oct-1-ene	1.2	4.5	18	67
Dec-1-ene	1.2	4.5	3.5	65
Dec-1-ene	5	4.5	3.5	80 (59)
Dodec-1-ene	5	7	2	83
11-Methoxyundec-1-ene	2	7	10	71
Styrene	1.2	2.5	1	99 (70)
4-Vinylcyclohexene	2	4.5	12	72[c]

[a] Duration of the addition of MeLi; [b] refluxing time after the end of addition of MeLi; [c] only the terminal double bond reacted.

a 5 molar equivalent excess of olefin led to isolation of the cyclopropane in 75% yield.

Complete regioselectivity was observed with vinylcyclohexene, only the external double bond being involved. This stands in striking contrast with other methods of methylenation which give mixtures with this diene [12]. A methoxy group away from the double bond was perfectly acceptable whereas vinyl or allyl ethers did not give the expected reaction.

With 1,2-disubstituted alkenes, the reaction was less efficient, as was to be expected from the above result with 4-vinylcyclohexene. Hept-2-ene (cf, table VII) gave practically no cyclopropanation under the conditions which had given a yield of 80% with terminal alkenes. *trans*-Stilbene gave an 87% yield of *trans*-1,2-diphenylcyclopropane; the *cis* isomer gave, less efficiently, a *trans/cis* mixture 30:70. The loss of specificity may be due to partial isomerization of the *cis* olefin in the reaction medium. Indeed, the recovered starting stilbene consisted of a mixture of isomers. Cyclic alkenes are apparently more reactive than acyclic alkenes: cyclooctene and one isomer of cyclododecene gave the cyclopropane compounds while norbornene gave only the *exo*-isomer. The yields compared favorably with those from other methods.

Table VII. Methylenation of 1,2-disubstituted alkenes with slowly generated *tert*-Bu-SO_2-CH_2Li (standard technique).

Alkene	*Equiv*	t_1 *(h)*[a]	t_2 *(h)*[b]	*Yield (%)*[c] *GLC (isolated)*
Hept-2-ene	5	7	10	<5
trans-Stilbene	1.2	7	8	87[d]
cis-Stilbene	1.2	7	8	41[e]
Cyclooctene	1.2	7	8	73
Cyclododecene[f]	5	5	19	25[g]
Norbornene	1.2	6	10	61[h,i]

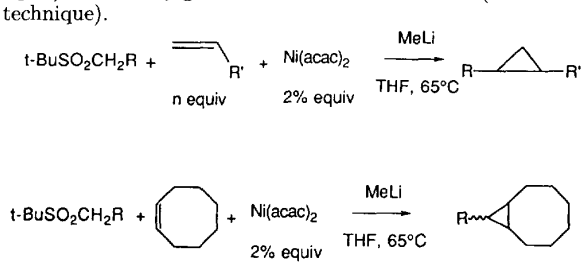
[a] Duration of the addition of MeLi; [b] refluxing time after the end of addition of MeLi; [c] GLC; the pure products were isolated by preparative GLC for identification; [d] only one isomer: *trans*-1,2-diphenyl cyclopropane was detected [13]; [e] 64% with 7 equiv alkene; [f] commercial mixture *cis/trans*; [g] *trans*-bicyclo [10.1.0]tridecane [13, 14]; [h] *exo*-tricyclo[3.2.1.$0^{2,4}$]octane [15]; [i] 95% with 5 equiv alkene.

With primary alkyl sulfones: alkylidenation of alkenes

The preliminary experiments demonstrated that primary alkyl sulfones could give a similar reaction. Since the formation of substituted cyclopropanes [15] is far less common than the methylenation, this reaction was studied in more detail.

With terminal alkenes, *tert*-butyl sulfones gave much better results than the corresponding aryl or symmetrical dialkyl sulfones. Thus, *tert*-butyl ethyl sulfone converted the alkenes into the corresponding methylcyclopropanes whereas *tert*-butyl pentyl sulfone gave the butylcyclopropanes in high yields even when practically 1 equiv of alkene was used. The reaction was usually run in refluxing THF although satisfactory results could be obtained at room temperature with excess olefin or a longer reaction time (table VIII). Longer alkyl sulfones could be used: *tert*-butyl dodecyl sulfone gave

Table VIII. Reaction of alk-1-enes and cycloalkenes (*n* equiv) with slowly generated *tert*-Bu-SO_2-CHLiR (standard technique).



R	*Alkene*	n	t_1 *(h)*[a]	t_2 *(h)*[b]	*Yield (%)*[c]	trans/cis
Me	Hex-1-ene	1.2	4.5	1.5	73	51:49
Me	Dec-1-ene	1.2	7	7	64	52:48
Me	Dodec-1-ene	5	7	7	83 (62)[d]	51:49
Me	Styrene	1.2	3	2	60	55:45
Me	Cyclooctene	1.2	10	6	30	97:3[f]
Me	Cyclooctene	15	10	6	52	96:4
Me	Norbornene	5	10	7	85 (56)[d]	57:43[g]
Bu	Cyclohexene	5	7	10	<5%	–
Bu	Cyclooctene	1.2	10	5	50	97:3
Bu	Cyclooctene	5	10	5	60(40)[d]	97:3
		15[e]			50	99:1
Bu	Norbornene	5	7	10	67	71:29[h]

[a] Duration of the addition of MeLi; [b] refluxing time after the end of addition of MeLi; [c] GLC; [d] the pure products were isolated by preparative glc for identification; [e] at 25 °C; [f] stereochemistry determined by NMR [16]; [g] methyl-tricyclo[(3.2.1.$0_{2,4}$)]octane *exo-exo/exo-endo*: 57:43 determined by ^1H and ^{13}C [17] NMR; [h] *exo-exo/exo-endo*: 71:29 determined by NMR by comparison with the methyl-substituted analog above.

the corresponding 1-undecyl-2 butylcyclopropane (52%, *trans/cis*: 49:51) with hex-1-ene.

Reaction of various cyclic alkenes with *tert*-butyl ethyl and *tert*-butyl pentyl sulfones was tried next. Cyclohexene proved to be very reluctant to the cyclopropanation whereas cyclooctene gave reasonable yields of the *exo* isomer very selectively. Norbornene was again very reactive.

The cyclopropanation did take place with acyclic internal olefins although much less efficiently. Except for stilbene, the yields were rather poor. Moreover mixtures of isomers were generally obtained. Even if the cyclopropanation reaction preserves the stereochemistry of the double bond, as suggested by the selectivity observed when symmetrical alkenes were used, the reaction conditions led to *Z* to *E* isomerization or even to migration of the double bond of alk-2-enes. In the latter case, the terminal olefins formed gave disubstituted cyclopropanes to a rather large extent due to the enhanced reactivity of monosubstituted alkenes. This isomerization of the alkene points to nickel(0) being present in the reaction, and the question arises of whether it is the actual catalyst in the cyclopropanation reaction.

With secondary alkyl sulfones

This would be of interest since it would lead to 1,1-disubstituted cyclopropanes. There are not many known