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A convenient preparation of mono- or *gem*-di-halogenoalkenes from α-sulfonyl carbanions and halogenolithiocarbenoïds

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Abstract

Various α-sulfonyl carbanions have been shown to react at low temperature with di- or tri-halogenolithiocarbenoïds, to give 1-mono- or 1,1-di-halogenoalkenes. Bromocarbenoïds gave better results than their chloro-analogues. Reaction of dibromolithiomethane with α-lithiated sulfones gives a high yield of vinylic bromides, the stereochemistry of which is cleanly *E*. Evidence is presented that the carbenoïd itself is responsible for the reaction, and is not first converted into the corresponding carbene.

Introduction

Both 1-mono- and 1,1-di-halogenoalkenes are useful reagents in organic syntheses. Whereas the latter are mainly encountered in powerful insecticides [1], the former are widely used, namely in substitution and coupling reactions leading to alkenes and dienes.

Several methods have been developed for preparation of these compounds. Vinylic halides are usually obtained by carbometalation of carbon–carbon triple bonds, followed by reaction with a halogenating agent (X_2, NBS, NCS...) [2]. Wittig and related reactions provide the most commonly used route to 1,1-dihaloalkenes [3], but other procedures, such as alkylation of trihalogenoalkenes [4] or alkylation/dehydrohalogenation of 1,1,1-trihalogeno derivatives, have been reported [5].

Two other methods attracted our attention, both involving the nucleophilic reaction of an ylid with an electrophilic species derived from treatment of trihalomethane by a base:

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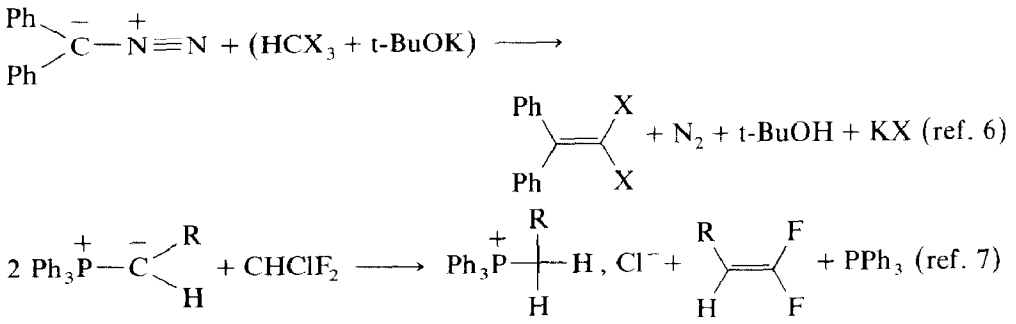


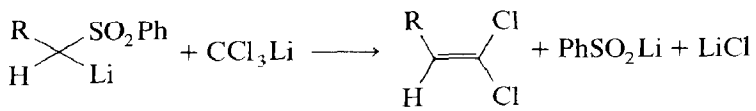
However, these reactions seem to be limited to a narrow range of compounds: the first one, which requires diazoalkanes stable at room temperature, is restricted to diphenylalkene preparation [6], while the second one has been used up to now only with difluoroalkenes [7].

We decided to investigate the feasibility of a similar reaction using readily available, thermally-stable, α-sulfonyl carbanions, instead of a diazoalkane or a phosphonium ylide.

Results and discussion

Reaction of α-sulfonyl carbanions with CX_3Li

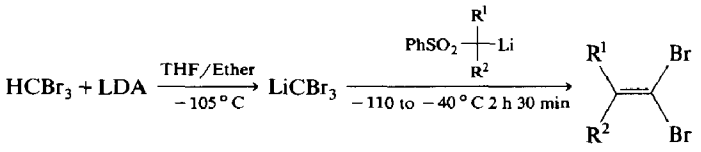
In the initial experiments chloroform was added at a temperature between −70 and 20 °C to a mixture of metalated sulfone with additional base (t-BuOK) or to a two-fold excess of lithiated sulfone, half of which would act as the base. Some of the expected dichloroalkene was formed, but yields were never above a few percent. We thus decided to use a very low temperature, so that the carbenoïd CCl_3Li could be generated by complete deprotonation of chloroform, without thermal decomposition, with the sulfonyl carbanion then added slowly. This carbenoïd has been reported to be stable up to −90 °C in THF [8]. Trichlorolithiomethane was thus prepared at −100 °C in pure THF, from chloroform and n-butyllithium, and lithiated phenyl heptyl sulfone added at this temperature. The reaction mixture was stirred for 1 h at −100 °C before being allowed to warm slowly to room temperature. However, the yield of 1,1-dichloro-1-octene remained very low (10%), much starting sulfone being recovered. Change of the solvent to a 50/50 THF/ethyl ether mixture, which allowed the reaction to be started at −110 °C before the slow warming up, led to an important increase in yield (58%).

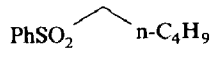
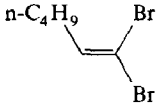
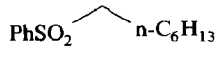
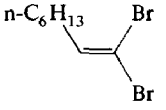
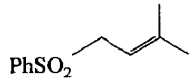
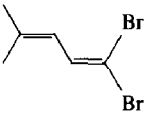
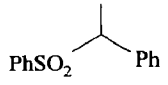
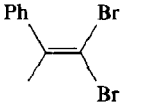
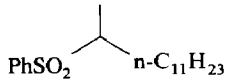
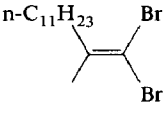


Unfortunately, all attempts to extend this approach to secondary alkyl or allyl sulfones met with failure, probably because of the impossibility of finding a temperature at which the carbenoïd is stable and still sufficiently reactive.

Similar reactions with CBr_3Li were much more successful; this carbenoïd which is known to be thermally stable up to −100 °C [9,10] can be generated either by metalbromine interchange from tetrabromomethane or metalation of bromoform. However bromine exchange would yield an alkyl bromide able to quench the

Table 1



Number	Sulfones	Products	Yields (%) (a)	(b)
1			80 [a]	66 [b]
2			85	67
3			45	37
4			71	60
5			79	67

[a] Determined by NMR of the crude reaction mixture with an internal standard. [b] Isolated yield after chromatography.

sulfonylcarbanion, and so metalation of $CHBr_3$ with lithium diisopropylamide (LDA) was preferred.

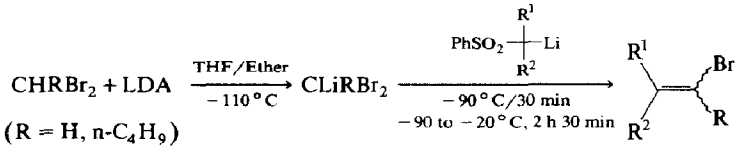
Deprotonation of bromoform was carried at −105 °C in THF/ether 50/50 for 40 minutes, and this was followed by slow addition at the same temperature of the cold (−78 °C) lithiated sulfone solution, with the reaction mixture finally allowed to warm slowly to room temperature.

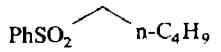
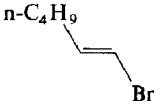
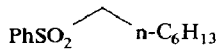
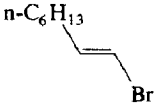
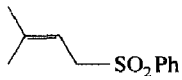
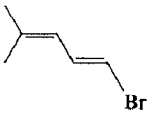
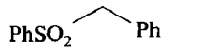
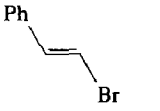
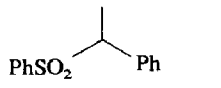
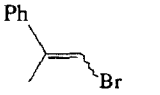
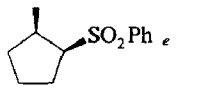
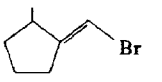
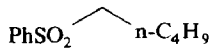
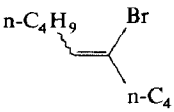
As shown in Table 1, yields are generally high, and the product can be easily separated from the starting sulfone (major impurity in the crude mixture) by a quick filtration through silica gel, making this method very competitive with those previously reported. The results obtained with secondary alkyl sulfones (runs 4 and 5) are particularly notable, since other methods are not so easily applicable to tetrasubstituted dibromo olefins (because of the much lower reactivity of ketones than of aldehydes).

Reaction of α-sulfonyl carbanions with $RCBr_2Li$

Villieras showed [10] that dibromolithioalkanes can be readily generated by metalation of the corresponding primary *gem*-dibromolkane by LDA, and are stable

Table 2



Number	Sulfones	Products	Yield	E/Z [c]
1			87 [a] [d]	88/12
2			86 [a] 81 [b]	88/12
3			70 [a] [d]	92/8
4			60 [a] 57 [b]	96/4
5			87 [a] 81 [b]	70/30
6	 [e]		80 [a] 78 [b]	92/8
7		 [f]	88 [a] 85 [b]	65/35

[a] determined by NMR of the crude reaction mixture with internal standard [b] isolated yield after chromatography [c] determined by both GLC and NMR [d] non isolated product, see Experimental section [e] same result starting from trans isomer; see text [f] R = n-C_4H_9

at −90 °C. By a procedure quite similar to that described above (see Experimental section for details of the relevant temperature), we were able to convert α-sulfonyl carbanions into 1-bromoalkenes in high yield.

The results shown in Table 2 demonstrate that the reaction works with any type of sulfone, primary and secondary alkyl as well as allylic and benzylic, and in this respect is widely applicable. In the case of primary sulfones (R_2 = H) and $CHBr_2Li$, the reaction is very stereoselective, giving the *E*-alkene as the major isomer. Surprisingly, the same result was observed (formation of *E*-isomer) with 2-methyl benzenesulfonylcyclopentane; the *E/Z* ratio was found to be independent of the stereochemistry (*cis* or *trans*) of the starting sulfone, which is related to the loss of stereochemistry induced by deprotonation, as shown by independent deuteration of the anion(s) from either sulfone which led to the *trans* deuterated sulfone only. Such

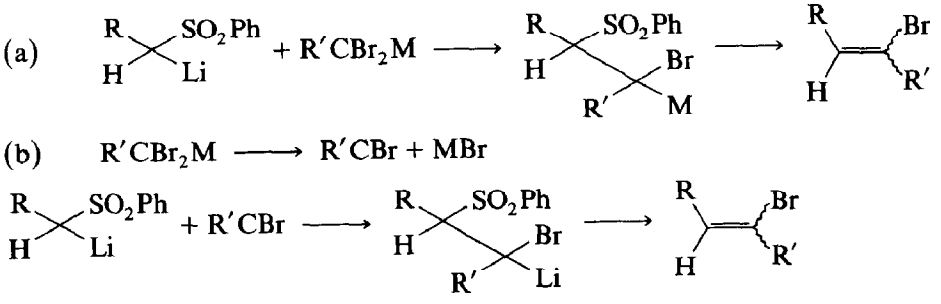
a loss of configuration is not general [11]. The *E* structure of the product was revealed by NMR spectroscopy including a nuclear Overhauser effect study.

Sodium and potassium halogenoalkanes have been far less studied than the lithium species. However Martel reported [12] that deprotonation of dibromomethane by sodium bis(trimethylsilyl)amide leads to a carbenoïd stable up to $-30\,^{\circ}C$, whereas the lithiated species is stable only below $-90\,^{\circ}C$ [8]. Reaction of lithiated phenyl heptyl sulfone with $NaCHBr_2$ at $-45\,^{\circ}C$ gave the expected bromoalkene in 87% yield and with an E/Z ratio of 61/39. The loss in stereoselectivity was shown not to be related to the temperature by repeating this experiment at $-68\,^{\circ}C$ (yield 39%, same stereochemistry: E/Z 61/39; at $-90\,^{\circ}C$ no reaction took place), but more probably to depend on the counter cation. Thus while use of sodium carbenoïds allows use of a more convenient temperature ($-45\,^{\circ}C$ instead of $-105\,^{\circ}C$), a poorer stereoselectivity must be expected.

Work is presently in progress to extend this new reaction to other carbenoïds, namely iodocarbenoïds, which should make possible the preparation of other functionalised alkenes from α-sulfonyl carbanions.

Nature of the electrophile

The account above shows clearly that olefin formation proceeds in high yield only when the α-sulfonyl carbanion is added to the metalated di- or tri-halogenoalkane at a temperature at which the latter is stable. This suggested that the sulfone anion reacts with the carbenoïd itself and not with the carbene formed via thermal decomposition, but more evidence was needed to decide between the two schemes a or b.



The stereoselectivity observed during the formation of the monobromoalkenes, together with the influence of the metal (Li, Na) on this stereoselectivity seems to favour scheme a. However better evidence for the operation of scheme a was provided by adding lithiated phenyl heptyl sulfone slowly to a cold ($-90\,^{\circ}C$) solution of $CHBr_2Li$ and stirring the mixture at this temperature for 3 h before quenching by ethanol at $-90\,^{\circ}C$, a 88% yield in 1-bromo-1-octene ($E/Z = 88/12$) being obtained. When for a comparison a solution of $CHBr_2Li$ was kept at $-90\,^{\circ}C$ for 3 h and the mixture then treated with iodomethane, 1,1-dibromoethane was formed quantitatively, showing that no decomposition of the carbenoïd to the carbene had taken place in the meantime, a result in good agreement with the observation by Villieras [10]. The same conclusion emerges from experiments with $NaCHBr_2$ at $-45\,^{\circ}C$, the carbene being formed only above $-30\,^{\circ}C$ [12].

The reaction described above is a new illustration of the electrophilic properties of α-metalated di- or tri-halogenoalkanes, which have been extensively studied by several groups [13].

Experimental

Pentane and petroleum ether were distilled from P_2O_5, dichloromethane from calcium hydride, and diethyl ether and THF from benzophenone radical anion. All reactions were carried out under pure nitrogen. Kieselgel Merck 60, 230–400 mesh ASTM was used for column chromatography.

The ^1H NMR spectra were recorded on Bruker 80 or 250 MHz spectrometers, the ^{13}C NMR spectra on a Bruker 100 MHz spectrometer, in $CDCl_3$ with Me_4Si as internal standard. A Nermag, R-10-10B instrument was used for mass spectra with electronic impact (EI) at 70 eV or with chemical ionization (NH_3).

Combustion analyses were performed by the "Service de microanalyse de l'Université Pierre et Marie Curie", Paris.

Sulfones

Primary alkyl phenyl sulfones, phenyl prenyl, and phenyl benzyl sulfones have been prepared by reaction of sodium benzenesulfinate with the corresponding halide in DMF and purified by filtration through alumina and recrystallisation from ether or ether/pentane mixtures.

Pentylsulfonyl benzene (phenyl pentyl sulfone) [Chem. Abstr. number 34009-04-6]: m.p. 31.5 °C, lit. [14] m.p. 28.7–31.6 °C.

Heptylsulfonyl benzene (phenyl heptyl sulfone) [52075-21-5]: m.p. 40 °C, lit. [15] m.p. 40 °C.

Phenylmethylsulfonyl benzene (phenyl benzyl sulfone) [3112-88-7]: m.p. 148 °C, lit. [16] m.p. 146 °C, lit. [17] m.p. 148–149 °C.

3-Methyl-2-butenylsulfonyl benzene (phenyl prenyl sulfone) [15874-80-3]: m.p. 54 °C, lit. [17] m.p. 54 °C.

α-Methylated alkyl sulfones were prepared by deprotonation (n-BuLi) of the corresponding primary sulfone in THF, followed by methylation of the carbanion (CH_3I).

1-Phenylethylsulfonyl benzene: m.p. 113 °C, lit. [18] m.p. 114 °C. ^1H NMR (80 MHz): 1.73 (d, *J* 7 Hz, 3H), 4.18 (q, *J* 7 Hz, 1H), 6.85–7.55 (m, 10H). MS(NH_3): 264(M + 18) 247(M + 1)105.

1-Methyldodecylsulfonyl benzene: m.p. 40–41 °C ^1H NMR (250 MHz): 0.86(t, *J* 6.5 Hz, 3H) 1.00–1.47 (m, 24H) 1.60–1.71(m, 1H) 1.82–2.01(m, 1H) 2.90–3.09(m, 1H) 7.46–7.67(m, 3H) 7.77–7.91(m, 2H). MS (NH_3): 342 (M + 18) 242 214. Anal. Found: C, 70.61; H, 9.88. $C_{19}H_{32}O_2S$ calcd.: C, 70.32; H, 9.93%.

The two isomers of 1-benzene sulfonyl-2-methyl cyclopentane were prepared as described by Truce [19]. Addition of thiophenol to methyl cyclopentene followed by oxidation of the sulfide gave the crude *cis* sulfone. Pure *cis* derivative was obtained by recrystallisation (ether/pentane). Treatment of the crude *cis* sulfone by sodium propanolate in propanol yielded the trans isomer.

cis-1-Benzenesulfonyl-2-methyl cyclopentane: m.p. 56–57 °C, lit. [19] m.p. 57–58 °C. ^1H NMR (250 MHz): 1.31 (d, *J* 7 Hz, 3H), 1.52–2.01 (m, 5H), 2.07–2.26 (m, 1H),

2.46–2.63(m, 1H), 3.44(m = q, 1H), 7.57–7.78(m, 3H) 7.93–8.03(m, 2H). MS (NH_3): 242(M + 18) 225(M + 1) 143 125.

trans-1-Benzenesulfonyl-2-methyl cyclopentane: m.p. 35.5 °C, lit. [19] m.p. 36.5–37.5 °C. ^{1}H NMR (250 MHz): 0.98(d, J 7 Hz, 3H), 1.28(m, 1H), 1.66(m, 2H), 1.94(m, 2H), 2.10(m, 1H), 2.50(m, 1H), 3.08(m, 1H), 7.56–7.76(m, 3H), 7.90–8.00(m, 2H). MS (NH_3): 242(M + 18), 225(M + 1).

Polyhalogenoalkanes

Dibromomethane, chloroform, and bromoform were purified by standard methods [20]. 1,1-Dibromopentane was prepared by alkylation of lithiodibromomethane with iodobutane [10] and purified by fractional distillation (b.p. 152–154 °C). All reactions were carried out in a 100 ml three-necked flask fitted with a thermometer, a septum, and nitrogen inlet. The apparatus was thoroughly cleaned and dried.

Reaction of $LiCCl_3$ with lithiated phenyl heptylsulfone: preparation of 1,1-dichloro-1-octene. To a stirred solution of freshly distilled chloroform (0.5 ml, 6.2 mmol) in diethyl ether/THF (7 ml/7 ml) at −110 °C was slowly added n-butyllithium (3.9 ml, 1.6 M in hexane, 6.2 mmol). The mixture was stirred for 45 min at −105 °C, changing from colourless to brown. A solution of lithiated sulfone was prepared independently at −78 °C from 6.2 mmol (1.49 g) of phenyl heptyl sulfone in 7 ml of THF and 3.9 ml of 1.6 M n-butyllithium in hexane, and the cold solution was then added slowly to the cold (−110 °C) solution of $LiCCl_3$. After the addition, the temperature was allowed to rise to −20 °C during 2.5 h. After protonation of any resulting carbanion by addition of ethanol (1 ml), followed by warming to room temperature and then hydrolysis with aqueous ammonium chloride, the mixture was extracted with dichloromethane, and the extract washed with water and dried over magnesium sulfate. The crude product obtained after evaporation of the extract was chromatographed to give the expected dichloroalkene 0.65 g yield 58%.

1,1-Dichloro-1-octene [1119-82-0], b.p. 64.5 °C/1.5 torr, lit. [21] b.p. 63 °C/1.5 torr. ^{1}H NMR (250 MHz): 0.84–1.00(m, 3H), 1.20–1.50(m, 8H), 2.18(m, 2H), 5.92(t, J 7 Hz, 1H), MS (EI)(relative intensity): 182(4.5) 180(11, M) 164(7) 162(32) 144(3, M − Cl) 128(8) 126(14) 111(30) 109 (100, $M - Cl_2$).

General procedure for the reaction of α-sulfonyl carbanions with $LiCBr_3$; formation of 1,1-dibromoalkenes

To a cold (−78 °C) stirred solution of distilled diisopropylamine (0.85 ml, 6 mmol) in diethyl ether (2 ml) was added butyllithium (3.75 ml, 1.6 M in hexane, 6 mmol). The temperature was then allowed to rise, and stirring was continued for 30 min at room temperature. The solution was again cooled to −78 °C and added slowly to a stirred solution of $HCBr_3$ (1.52g, 6 mmol) in diethyl ether/THF mixture (7 ml/7 ml) at −105 °C. Stirring was continued for 40 min at −105 °C, during which the colourless solution turned pale yellow. A solution of lithiated sulfone was prepared independently at −78 °C from 6 mmol of sulfone in the minimum amount of THF (the volume is indicated below) and 3.75 ml of 1.6 M n-butyllithium in hexane. Stirring was continued for 30 min at room temperature. This solution was cooled at −78 °C and then added slowly through a canula to the cold (−110 °C) solution of carbenoïd. After the addition, the temperature was allowed to rise to −50 °C during 45 min, during which the lemon yellow solution turned brown yellow. After protonation of any resulting carbanion by addition of ethanol (0.5 ml),

hydrolysis by aqueous saturated ammonium chloride solution (10 ml), extraction with methylene chloride, and washing of the extract once with water, and drying over magnesium sulfate, solvent was evaporated off and the residue chromatographed on a small column of silica gel (pentane/methylene chloride) to give 1,1-dibromo olefin and starting sulfone.

1,1-Dibromo 1-hexene [73383-23-0] from phenyl pentyl sulfone (in THF 15 ml). Yield: 80%. ^{1}H NMR (250 MHz): 0.90(m, 3H), 1.19–1.50(m, 4H), 2.10(m, 2H), 6.45(t, *J* 7 Hz, 1H), in agreement with lit. [22]. MS (EI)(relative intensity): 243(16) 241(34, $M-1$) 239(18) 215(27) 213(33) 211(13) 201(48) 199(99) 197(57) 179(97.5) 177(100) 161(25, M-Br) 159(22) 151(35) 149(43) 140(63) 138(61).

1,1-Dibromo 1-octene [73383-25-2] from phenyl heptyl sulfone (in THF 5 ml). Yield: 85%. ^{1}H NMR (250 MHz): 0.89(m, 3H), 1.20–1.42(m, 8H), 2.10(m, 2H), 6.44(t, *J* 7 Hz, 1H), in agreement with lit. [22]. MS (NH_3): 272 270(M) 268 225 223 212 199 195 189($M-$Br) 187 140 138 133 131 125 115 107.

1,1-Dibromo 4-methyl 1,3-pentadiene [64305-70-0] from phenyl prenyl sulfone (in THF 9 ml). Yield: 45%. ^{1}H NMR (250 MHz): 1.76(s, 3H), 1.80(s, 3H), 5.85(dm, *J*(=CH-CH=) 10.5 Hz, 1H), 7.10(d, *J*(=CH-CH=) 10.5 Hz, 1H). ^{13}C NMR: 19.32 (CH_3), 26.29(CH_3), 88.53(=C<), 122.20(=CH), 133.54(CH=), 140.78(>C=). MS (NH_3): 242 240(M) 238.

(2,2-Dibromo, 1-methylethenyl)benzene [60014-86-0] from 1-phenylethylsulfonyl ben-zene (in THF 36 ml). Yield: 71%. ^{1}H NMR (80 MHz): 2.18(s, 3H) 7.05–7.43(m, 5H), in agreement with lit. [23]. MS (NH_3): 278 276(M) 274 197 195($M-$Br) 116 115($M-Br_2$)

1,1-Dibromo 2-methyl tridecene from 1-methyldodecylsulfonyl benzene (in THF 5 ml). Yield: 79%. ^{1}H NMR (250 MHz): 0.88(m, 3H), 1.20–1.54(m, 18H), 1.89(s, 3H), 2.28(m, 2H). MS (EI)(relative intensity): 356(12) 354(24, M) 352(12) 193(28, $M-Br_2$) 191(20) 137(22) 123(44) 109(75) 95(100) 81(87). Found: C, 47.63; H, 7.46. $C_{14}H_{26}Br_2$ calcd.: C, 47.48; H, 7.40%.

General procedure for reaction of α-sulfonyl carbanions with $LiCHBr_2$: formation of 1-bromo-1-alkenes

To a stirred solution of distilled diisopropylamine (0.71 ml, 5 mmol) in diethyl ether/THF mixture (7 ml/10 ml) at −78 °C was added butyllithium (3.1 ml, 1.6 *M* in hexane, 5 mmol). Stirring was continued at room temperature for 30 min and the solution was then cooled at −90 °C and a solution of dibromomethane (0.35 ml, 5 mmol) in THF (5 ml) at −78 °C was slowly added. Stirring was continued at −90 °C for 30 min, during which the colourless solution turned yellow. A solution of lithiated sulfone was prepared independently at −78 °C from 5 mmol of sulfone in the minimum amount of THF (the volume is indicated below) and 3.13 ml of 1.6 *M* n-butyllithium in hexane. Stirring was continued for 30 min at room temperature (except for phenyl benzyl sulfone). This solution was cooled at −78 °C and then added slowly through a canula to the cold (−100 °C) solution of carbenoïd. After addition, the temperature was allowed to rise to −20 °C in 2 h 30 min. Work-up as above gave the 1-bromo olefin and sulfone.

1-Bromo-1-hexene: *E*[13154-13-7], *Z*[13154-12-6] from phenyl pentyl sulfone (in THF 15 ml). Yield: 87% $E/Z = 88/12$. ^{1}H NMR (250 MHz): *E*: 0.82–0.92(m = t, 3H), 1.16–1.48(m, 4H), 2.06(q, *J* 7 Hz, 2H), 6.07(d, *J* 14 Hz, 1H, =CHBr),

6.20(m = dt, J_d 14 Hz, J_t 7 Hz, 1H, C-CH=), in agreement with lit. [24]. MS (NH_3): *E*: 164 162(M) 138 136 121 119 102 100.

1-Bromo-1-octene: *E*[51751-87-2], *Z*[42843-49-2] from phenyl heptyl sulfone (in THF 5ml). Yield: 86% *E*/*Z* = 88/12. ^{1}H NMR (250 MHz): *E*: 0.81–0.94(m = t, 3H), 1.18–1.48(m, 8H), 2.03(q, *J* 7 Hz, 2H), 6.05(d, *J* 14 Hz, 1H, =CHBr), 6.23(m = dt, J_d 14 Hz J_t 7 Hz, 1H, C-CH=), in agreement with lit. [25]. MS (NH_3): *E*: 192 190(*M*) 152 136 128 124 121 119 110; *Z*: 192 190(*M*) 152 136 128 124 121 119 110.

1-Bromo-4-methyl-1,3-pentadiene: from phenyl prenyl sulfone (in THF 8 ml). Yield: 70% *E*/*Z* = 92/8. ^{1}H NMR (250 MHz): *E*: 1.71(s, 3H) 1.75(s, 3H) 5.75(dm, *J*(=CH-CH=) 11.3 Hz, 1H), 6.14(d, *J*(CH=CHBr) 13.2 Hz, 1H), 6.91(dd, *J*(CH=CHBr) 13.2 Hz *J*(=CH-CH=) 11.3 Hz, 1H), *Z*: 1.78(s, 3H), 1.84(s, 3H), 5.75(dm, 1H), 6.05(d, *J*(CH=CHBr) 8.5 Hz, 1H), 6.80(dd, *J*(CH=CHBr) 8.5 Hz, *J*(=CH-CH=) 6.25 Hz, 1H). ^{13}C NMR: *E*; 18.37(CH_3) 25.85(CH_3) 105.80(CH) 122.42(CH) 134.19(CH) 137.01 (>C=). MS (NH_3): *E*: 162 160(*M*) 121 119 100. Highly sensitive substance [23]: no satisfactory microanalysis.

2-Bromoethenyl-benzene(β-bromostyrene): *E*[588-72-7], *Z*[588-73-8] from phenyl benzyl sulfone (in THF 30 ml). Yield: 60% *E*/*Z* = 96/4. ^{1}H NMR (80 MHz): *E*: 6.58(d, *J* 13 Hz, 1H, =CHBr) 6.97(d, *J* 13 Hz, 1H, =CHPh) 7.05–7.33(m = s, 5H, Ph), in agreement with lit. [26]. MS (NH_3): *E*: 184 182(M) 120 103, *Z*: 184 182(M) 130 120 112 103.

(2-Bromo-1-methylethenyl)-benzene: *E*[16917-35-4], *Z*[19647-26-8] from 1-phenyl-ethylsulfonyl benzene (in THF 30 ml). Yield: 87% *E*/*Z* = 70/30. ^{1}H NMR (250 MHz): *E*: 2.22(d, *J* 1.5 Hz, 3H) 6.48(q, *J* 1.5 Hz, 1H). 7.30–7.48(m, 5H), in agreement with lit. [27]; *Z*: 2.11(d, *J* 1.5 Hz, 3H), 6.25(q, *J* 1.5 Hz, 1H), 7.30–7.48(m, 5H), in agreement with lit. [27]. MS (NH_3): *E*: 198 196(*M*) 134(*M* − Br + 18) 117(*M* − Br) 115; *Z*: 198 196(*M*) 134(*M* − Br + 18) 117(*M* − Br) 115.

1-Methyl-1-bromomethylene-cyclopentane from 1-benzenesulfonyl-2-methyl cyclopentane (in THF 9 ml). Yield: 80% *E*/*Z* = 92/8. ^{1}H NMR (250 MHz): *E*: 1.09(d, *J* 7 Hz, 3H), 1.20–1.41(m, 1H), 1.51–1.70(m, 1H), 1.73–1.90(m, 1H), 1.91–2.06(m, 1H), 2.25–2.56(m, 3H), 5.87–5.93(m, 1H). ^{13}C NMR: *E*: 18.38(CH_3), 23.38(CH_2), 33.29(CH_2), 36.31(CH_2) 40.45(CH), 97.31(=CHBr), 154.47(C). MS (NH_3): *E*: 192(*M* + 18) 176 174(*M*) 161 159 148 146 136 129 119 112; *Z*: 192(*M* + 18) 176 174(*M*) 163 148 146 136 128 112. Anal. Found: C, 48.21; H, 6.53. $C_7H_{11}Br$ calcd.: C, 48.02; H, 6.33%.

5-Bromo-5-decene *E*[72612-74-9], *Z*[72612-75-0] from phenyl pentyl sulfone (in THF 15 ml). Yield: 88% *E*/*Z* = 65/35. ^{1}H NMR (250 MHz): mixture of isomers: 0.80–1.02(m, 6H), 1.05–1.68(m, 8H), 1.96–2.10(m, 4H, CH_2–C=*E*), 2.10–2.24(m, 4H, CH_2–C=*Z*), 5.76(t, *J* 7 Hz, 1H, CH=*Z*), 5.90(t, *J* 7 Hz, 1H, CH=*E*), in agreement with lit. [28]. MS (NH_3): *E*: 220 218(M) 178 176(*M* − C_3H_6) 164 162(*M* − C_4H_8) 156(*M* − Br + 18) 138 120 109; *Z*: 220 218(*M*) 178 176(*M* − C_3H_6) 164 162(*M* − C_4H_8) 156(*M* − Br + 18) 138 120 109.

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