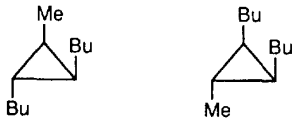
Table IX. Reaction of alkenes (n equiv) with slowly generated *tert*-Bu-SO_2-CH(Li)R (standard technique).



trans **A** *trans* **B**

R	*Alkene*	n *(equiv)*	t_1 *(h)*[a]	t_2 *(h)*[b]	*Yield (%)*[c]	trans/cis
Me	(*E*) Dec-5-ene	1.2	10	6	15	*trans* A
Me	(*E*) Dec-5-ene	5	10	6	22 (16)[d]	*trans* A
Bu	(*E*) Dec-5-ene	5	10	7	25	*trans*[e]
Bu	(*E*) Hept-2-ene	1.2	10	10	19[f]	A/B = 11:8
					14[g]	7/7
Bu	(*Z*) Hept-2-ene	1.2	10	10	10[f,h]	A/B = 9:1
					30[g,h]	15:15
Bu	*trans*-Stilbene	1.2	10	10	50	*trans*[e]

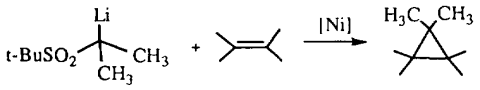
[a] Addition of MeLi; [b] further refluxing; [c] GLC; the pure products were isolated by preparative GLC for identification; [d] isolated yield; [e] one isomer formed; the *trans* stereochemistry was established by proton and carbon NMR; [f] 1,2-dibutyl-3-methylcyclopropane (two isomers); [g] 1-butyl-2-pentyl cyclopropane (two isomers), see text; [h] some (*E*) hept-2-ene was found showing that stereoisomerization of the starting alkene had taken place under the reaction conditions.

ways to convert a double bond into a *gem*-disubstituted cyclopropane [15, 18–20, 27]. Many natural products have a *gem* dimethylcyclopropane unit in their structure, and this fact led us to investigate the reactivity of isopropyl sulfone.

Since styrene had proved more reactive than aliphatic alkenes, it was used for the first experiments. In fact using a small excess (1.2 equiv) it was converted by *tert*-butyl isopropyl sulfone into the desired cyclopropane compound in 83% yield: even diisopropyl sulfone could be used (70% yield). The sulfone is very readily available by oxidation of the commercial diisopropyl sulfide.

Aliphatic terminal alkenes could also be converted by *tert*-butyl isopropyl sulfone into dimethyl cyclopropyl compounds, although the yields were much lower than with styrene. Even when using excess alkene the yields were only about 30% (table X). Cyclooctene gave similar results. The use of nickel bromide did not improve the yields.

Table X. *gem*-Dimethylcyclopropanation of alkenes with slowly generated lithiated *tert*-butyl isopropyl sulfone (standard technique).



Alkene	n *(equiv)*	t_1 *(h)*[a]	t_2 *(h)*[b]	*Yield (%)*[c]
Styrene	1.2	2.5	1	83 (59)[d]
1-Phenylprop-1-ene	5	10	8	31[e]
Dec-1-ene	1.2	10	10	15
Dec-1-ene	10	10	10	32[f]
Cyclooctene	12	10	8	30

[a] Addition of MeLi; [b] further refluxing; [c] GLC; [d] the pure product were isolated by preparative GLC for identification; [e] one isomer only; *trans* stereochemistry from ^1H and ^{13}C NMR spectra [21]; [f] some 2-methyldodec-2-ene was formed.

Fair to good yields of *gem*-dimethylcyclopropanes can be obtained by this simple technique. In some cases an aliphatic 2-methylalk-2-ene, isomeric with the expected cyclopropane, was also formed.

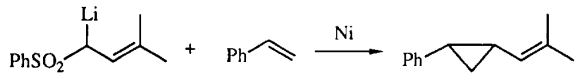
With allylic sulfones

The cyclopropanation reaction with allylic sulfones should lead to vinyl cyclopropanes. These are of interest [22] as such (pyrethroids), but also because they can be converted into cyclopentenes [23]. Alternatively they can be used in ring opening [24] or ring expansion [25] or cycloadditions reactions [26].

Vinyl cyclopropanes can be prepared by treatment of alkenes with vinyldiazoalkanes [27] or with other vinylcarbenoids [27, 28]. For indirect methods see reference [29]. The formation of cyclopropanes in the reaction of metallated allylic sulfones with electron-deficient alkenes is well known [30].

The reaction was tried with *tert*-butyl prenyl sulfone and styrene (MeLi); it gave less than 5% of the expected product. Apart from the triene formed by homocoupling [5, 7] (8%), a compound was obtained which proved to be a vinylcyclopropyl sulfone. This had been obtained previously by treatment of phenyl prenyl sulfone with base: isomerization of the allylic into the vinylic group would provide an electron-deficient double bond ready for cyclopropanation by another molecule of allylic sulfone [7, 31].

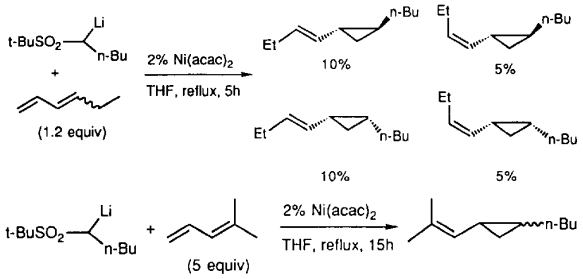
Phenyl prenyl sulfone gave the same result. However, since the isomerization of the starting sulfone needs the presence of non-metallated sulfone, the technique was changed in that now the pre-metallated sulfone was slowly added to a solution of $Ni(acac)_2$ and styrene in THF. The expected cyclopropane was then obtained in 21% yield (*trans/cis*: 84:16).



tert-Butyl methallyl sulfone, however, gave only an 8% yield of the expected vinylcyclopropane with styrene (*trans/cis*: 83:17).

Another approach to vinylcyclopropanes is the cyclopropanation of conjugated dienes [32a], for instance with sulfonium ylids [32c]. It was mentioned above that the more substituted double bonds were much less reactive in the cyclopropanation reaction so that some regioselectivity could be expected (as in the above-mentioned reaction of vinyl cyclohexene).

On treatment with *tert*-butyl pentyl sulfone (standard conditions) hexa-1,3-diene (commercial mixture of the stereomers, 1.2 equiv) gave a mixture of four stereomers formed by regioselective reaction of the terminal double bond in a total yield of 30%.



Similarly 4-methylpenta-1,3-diene gave regioselectively the cyclopropanation of the primary double bond (62%; *trans/cis*: 40:60).

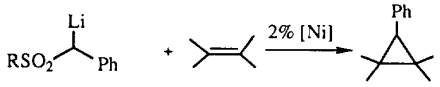
The same cyclopropane has been obtained by treatment of hex-1-ene with prenyl bromide and lithium tetramethylpiperidide (LiTMP) [28d]. This technique had proved more efficient with more substituted double bonds so the techniques are complementary.

With benzylsulfones

Alkenes have been converted into phenylcyclopropanes with phenyl diazomethane [33], diiodotoluene and diethylzinc [34], benzyl chloride and LiTMP [35] or several metal carbene complexes [36]. It was mentioned above that the formation of triphenylcyclopropane on treatment of phenyl benzyl sulfone with base in the presence of $Ni(acac)_2$ had led us to carry out this study. *tert*-Butyl and phenyl benzyl sulfone were therefore compared in the cyclopropanation of alkenes. Some results are collected in table XI.

Phenylcyclopropanes were indeed formed in moderate yields and styrene was once again more reactive than the aliphatic alkenes, for which sizable amounts of stilbene and triphenylcyclopropane were found. It is remarkable that with benzyl sulfones the phenyl residue compared favorably with the *tert*-butyl.

Table XI. Cyclopropanation of alkenes with slowly generated Ph-SO_2-CH(Li)-Ph and *tert*-Bu-SO_2-CH(Li)-Ph (standard technique).



Alkene	*Equiv*	t_1 *(h)*[a]	t_2 *(h)*[b]	*Cyclopropane GC yield (%)* *R = Ph*	trans/cis[c]	*R = t-Bu*	trans/cis[c]
Hex-1-ene	2	7	12	35[d]	50:50	30[e]	50:50
Hex-1-ene	10	7	12	56	50:50	44	50:50
Styrene	1	3	10	72	52:48	–	
Cyclohexene	10	10	10	22[f]	99:1	11[g]	99:1
Cyclooctene	10	7	10	43	96:4	–	

[a] Addition of MeLi; [b] further refluxing; [c] *trans/cis* or *exo/endo*; [d] stilbene (34%) and triphenyl cyclopropane (8%) were found; [e] stilbene (27%) and triphenyl cyclopropane (20%); [f] stilbene (36%) and triphenyl cyclopropane (14%); [g] stilbene (21%) and triphenylcyclopropane (32%).

Discussion

The results presented in this work show that under nickel catalysis lithiated sulfones (methyl, primary alkyl, secondary alkyl, benzyl) can convert alkenes into cyclopropanes. The reaction has been shown to be much more efficient for monosubstituted alkenes, which can lead to regioselectivity in the case of dienes. The known ways of achieving such a conversion [12] include the Simmons–Smith reaction [37a], the use of diazoalkanes [37b] and stoichiometric reactions of transition metal carbenes complexes [36, 38, 40] or carbenoids derived from alkali metals [27, 28, 39, 40].

Two remarks should be made. First, as regards the stereochemical result of these reactions, a striking difference appeared with cyclic alkenes. Whereas the known methods gave variable proportions of the *exo/endo* isomers with a more or less marked excess of the *endo* isomer, the new reaction gave a large excess of the other, *exo* isomer, often nearly 100%. In table XII, we compare the stereochemical results of the phenylcyclopropanation with the various techniques.

Second, the new reaction has a definite preference for the less substituted double bonds whereas the known methods gave better results with more substituted ones.

Table XII. Stereochemistry of phenylcyclopropanes obtained via phenylmethylene group transfer.

Methods	*Alkene*	*Cyclopropane*	exo/endo
$RSO_2CH(Li)Ph^a/Ni(acac)_2$	Cyclohexene	25	99:1
$RSO_2CH(Li)Ph^a/Ni(acac)_2$	Cyclooctene	25	96:4
$PhCH_2I_2/Et_2Zn$ [34]	Cyclohexene	69	13:87
		68	6:94
$PhCH_2N_2/ZnCl_2$ [33]	Cyclohexene	90	26:74
$PhCH_2Cl$/LiTMP [35a]	Cyclohexene	53	31:69
$(CO)_5W{=}CHPh$ [21]	Cyclopentene	40	38:62
$[Cp(CO)_2Fe{=}CHPh]^+$ [40]	Cyclopentene	78	1:200

[a] R = *t*-Bu, Ph.

The reagents involved are considered as electrophilic. In order to bring more quantitative data into this discussion, the Hammett technique can be used, as has been done with other cyclopropane-forming reactions [41–43].

para-Substituted styrenes (chloro, fluoro, hydrogen, methyl, methoxy) were treated with *tert*-butyl methyl sulfone and $Ni(acac)_2$. The data are given in the *Experimental section*. A good correlation was obtained and a ρ value of +1.90 was found. This should be compared with the values found for the Simmons–Smith reaction (−1.61 [41c]), the iron carbene complex (−2.2 [42b]), the mercury carbenoid (−0.619 [43b]) and the potassium carbenoid (−0.58 to −1.06, [43e]).

Obviously, the electronic character of the nickel-catalyzed cyclopropanation with sulfones is the opposite of that of the known reactions. It appears to be nucleophilic. It should perhaps be recalled in this respect that the cyclopropanation with diazoalkanes [33] or bicyclobutane [44] or 1,1-dimethoxycyclopropene [45] catalyzed by nickel (0) only worked with electron-deficient alkenes (see, however, reference [46]).

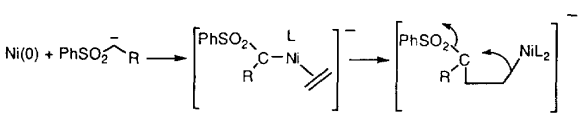
Finally it has been mentioned that Ni(0) is present in the reaction mixture as shown by the isomerization of the alkene used. Its role as the actual catalyst in the reaction should be considered. It is in agreement with the superiority of *Technique E* where the nickel species are exposed to the BuLi or MeLi and therefore can be reduced. In fact when treating $Ni(acac)_2$ first with BuLi, which should convert it into Ni(0) before the cyclopropanation, the same results were obtained. Further when using the $Ni(cyclooctadiene)_2$ complex the same results were obtained [47].

This led us to wonder about the coordination of the alkene to the metal. This has been shown to influence the efficiency and selectivity of cyclopropane formation with diazoesters [48]. A strong correlation can be seen (table XIII) between the yield of the cyclopropane compound formed and the association constant of the alkene with Ni(0). Therefore the reagent combination should not necessarily be regarded as nucleophilic but as an organometallic reagent.

Table XIII. Yields of cyclopropanation compared to the dissociation constants [49] of the alkene Ni(0) complexes.

Alkene	K	*Yield*
Styrene	10	60–90
Hex-1-ene	1.4	92
Norbornene	4.4	67
Cyclooctene	6.2×10^{-2}	60
Ethyl vinyl ether	3.0×10^{-3}	
Hex-2-ene *E*	2.7×10^{-3}	
Hex-2-ene *Z*	2.8×10^{-3}	
2-Methylpent-1-ene	1.2×10^{-3}	25
Cyclohexene	3.5×10^{-4}	<5

This suggests a tentative mechanism. Let us assume that the α-sulfonylcarbanion can act as a Ni(0) ligand [50], forming an ate complex of Ni(0); some nickelates of this kind have actually been isolated [51]. Insertion of the alkene between this ligand and nickel would lead to a situation where an organometallic carbon atom sits in the 1,3-position with regard to the sulfonyl-substituted carbon atom. It is known that this leads to



cyclopropane ring formation [30a]. Further investigation of this mechanism is underway.

Experimental section

Mass spectra were obtained on a Nermag R10-10B spectrometer via direct introduction by chemical ionization with ammonia (CI, NH_3), GLC-MS using a capillary column (CPSIL-5 CB, 50 m × 0.32 mm). Melting points were determined on a Buchi 510 capillary apparatus and uncorrected. ^{1}H-NMR spectra were recorded on a Cameca 250 or on a Bruker AM 400 instrument.

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). When J-mod method spectra were utilized, $-CH_3$ and -CH are indicated by +; $-CH_2$ and -C are indicated as −. When ^{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, $-CH_3$). Infrared spectra were obtained on a Perkin Elmer 599 instrument. Microanalyses were performed by the analytical laboratory of the Université Pierre-et-Marie-Curie.

Preparation of the starting sulfones

tert-Butyl alkyl sulfides were obtained by phase-transfer-catalyzed alkylation of sodium *tert*-butyl mercaptide; they were oxidized to the corresponding sulfones either by hydrogen peroxide or by sodium perborate [7].

tert-Butyl methyl, ethyl, pentyl, dodecyl sulfones have been described recently [7].

tert-Butyl isopropyl sulfone [69489-93-6]: mp 44–45 °C.

tert-Butyl prenyl sulfone: mp 42 °C.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 1.40 (s, 9H), 1.72 (s, 3H), 1.80 (s, 3H), 3.72 (br d, J = 7.5 Hz, 2H), 5.3 (br t, J = 7.5 Hz, 1H).

^{13}C-NMR ($CDCl_3$): δ 18.28 (CH_3), 25.51 (CH_3), 25.84 (CH_3); 46.71 (C), 59.32 (CH_2), 109.60 (CH), 141.89 (C).

MS (NH_3, DCI) m/z: 208 (M^+ + 18), 191 (M^+ + 1).

Anal calc for $C_9H_{18}O_2S$: C, 56.80: H, 9.53. Found: C, 56.97; H, 9.48.

Alkenes used in the cyclopropanation reactions

Most of the olefins used are commercial chemicals and were used without further purification. 11-Methoxyundec-1-ene [7289-47-6] was prepared according to reference [52]. Nickel acetylacetonate (Merck, 98%, water 0.5%) was dried under reduced pressure (0.1 mbar) at 50 °C for several hours.

General procedure for cyclopropanation reactions (standard technique)

The sulfone (3.33 mmol) and nickel acetylacetonate (17 mg, 0.02 equiv) were dissolved in anhydrous THF (7 mL). The appropriate amount of the selected olefin was then introduced and the mixture was stirred and refluxed. Methyllithium (3.33 mmol, 1.6 M in diethyl ether) was slowly added

over a period of 2 to 10 h using a syringe pump. The mixture was then kept refluxing for a few hours (see text and tables). It was cooled to room temperature, hydrolyzed with a saturated aqueous solution of ammonium chloride and extracted with dichloromethane. The combined organic layers were washed with water, dried over anhydrous magnesium sulfate and concentrated in vacuo. Flash chromatography (silica gel/pentane) gave a mixture of hydrocarbons. Analytically pure samples of cyclopropanes were obtained by preparative GLC.

Preparative scale methylenation of dodec-1-ene. Isolation of the product after oxidation of the remaining alkene [53]

The crude mixture of hydrocarbons obtained after reaction of tert-butyl methyl sulfone (6.66 mmol, 905 mg) and dodec-1-ene (1.5 molar equiv, 2.21 mL) according to the general procedure described above, was treated with sodium perborate (13.3 mmol, 3.2 g) and ruthenium trichloride hydrate (15 mg) in a mixture of acetonitrile (20 mL), carbon tetrachloride (20 mL) and water (30 mL). The oxidizing mixture was stirred at room temperature for 2 h. After evaporation of the organic solvents, the residue was extracted with dichloromethane. Ordinary work-up and flash chromatography (silica gel, pentane) gave *n*-decylcyclopropane (803 mg, 66%).

Characterization of the cyclopropane products

- *From* tert-*butyl methyl sulfone*

Phenylcyclopropane [873-49-4], *n*-hexylcyclopropane [4468-61-5], *n*-octylcyclopropane [1472-09- 9] and *n*-decylcyclopropane [5794-39-8] were prepared by cyclopropanation of styrene, oct-1-ene, dec-1-ene and dodec-1-ene, respectively. The spectra were in agreement with references [21, 13, 54].

■ *(9-Methoxynonyl)cyclopropane (methyl 9-cyclopropylnonyl ether)*

Prepared from 11-methoxyundec-1-ene.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.00 (m, 2H), 0.39 (m, 2H), 0.65 (m, 1H), 1.19 (q, J = 7 Hz, 2H), 1.27–1.43 (m, 14H), 1.54–1.62 (m, 2H), 3.34 (s, 3H), 3.38 (t, J = 7.0 Hz, 2H).

^{13}C-NMR ($CDCl_3$): δ 4.30 ($2CH_2$), 10.85 (CH), 26.12 (CH_2), 29.49 (CH_2), 29.57 (CH_2), 29.61 (CH_2), 29.62 (CH_2), 34.75 (CH_2), 58.44 (CH_3), 72.93 (CH_2).

MS (DCI, NH_3) m/z: 216 (M^+ + 18), 199, 166, 109.

Anal calc for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found C, 79.04; H, 13.21.

■ *4-Cyclopropylcyclohexene [80105-51-7]*

Prepared from 4-vinylcyclohexene.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.12 (m, 2H), 0.45 (m, 2H), 0.60–0.75 (m, 1H), 1.4–1.5 (m, 1H), 1.7–2.20 (m, 6H), 5.70 (m, 2H).

^{13}C-NMR ($CDCl_3$): δ 2.76 (CH_2), 2.99 (CH_2), 16.70 (CH), 25.07 (CH_2), 28.43 (CH_2), 31.39 (CH_2), 38.85 (d, CH), 126.45 (CH), 126.75 (CH).

MS (EI) m/e (Relative intensity): 122 (M^+), 107 (2), 93 (15), 79 (100), 77 (43), 67 (57), 65 (25), 53 (65).

■ *Bicyclo[6.1.0]nonane [286-60-2]*

Prepared from *cis*-cyclooctene. The spectra were in agreement with reference [13].

^{1}H-NMR ($CDCl_3$, 250 MHz): δ −0.29 (m, 1H), 0.50–0.68 (m, 3H), 0.82–1.0 (m, 2H), 1.30–1.75 (m, 8H), 1.9–2.05 (m, 2H).

^{13}C-NMR ($CDCl_3$): δ 9.74 (CH_2), 15.43 (2CH), 26.66 ($2CH_2$), 27.19 ($2CH_2$), 29.87 ($2CH_2$).

MS (EI) m/z (relative intensity): 124 (M^+, 17), 109 (5), 96 (63), 81 (74), 67 (100), 54 (71).

Anal calc for C_9H_{16}: C, 87.00; H, 12.99. Found: C, 87.05; H, 12.97.

■ trans-*Bicyclo[10.1.0]tridecane [15840-80-9]*

Prepared by cyclopropanation of cyclododecene (commercial mixture of *cis* and *trans* isomers).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.20 (t, J = 6.5 Hz, 2H), 0.50–0.70 (m, 4H), 1.30–1.45 (m, 12H), 1.50–1.65 (m, 4H), 1.94–2.02 (m, 2H), in agreement with reference [14].

^{13}C-NMR ($CDCl_3$): δ 14.05 (CH_2), 17.27 (2CH), 23.31 ($2CH_2$), 24.34 ($2CH_2$), 27.48 ($2CH_2$), 27.90 ($2CH_2$), 33.28 ($2CH_2$).

MS (EI) m/z (relative intensity): 180 (M^+), 109 (17), 96 (48), 82 (76), 67 (81), 55 (100).

Anal calc for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.50; H, 13.52.

■ cis-*Bicyclo[10.1.0.]tridecane [13757-44-3]*

^{1}H-NMR ($CDCl_3$, 250 MHz): δ −0.29 to −0.40 (m, 1H), 0.46–0.76 (m, 3H), 0.82–1.80 (m, 20H).

^{13}C-NMR ($CDCl_3$): δ 10.15 (CH_2), 16.78 (2CH), 22.66 ($2CH_2$), 25.92 ($2CH_2$), 26.96 ($2CH_2$), 27.55 ($2CH_2$), 25.58($2CH_2$), in agreement with references [13, 14].

■ exo-*Tricyclo[3.2.1.$0^{2,4}$]octane [13377-46-3]*

Prepared from norbornene.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ −0.13 (q, J = 7.0 Hz, 1H), 0.27 (m, 1H), 0.58 (d br, J_{ab} = 10.0 Hz, 1H), 0.65 (dd, J_1 = 7.0 Hz, J_2 = 3.0 Hz, 2H), 0.90 (d-quin, J_{ab} = 10.0 Hz, J_{quin} = 2.0 Hz, 1H), 1.24 (m, 2H), 1.42 (m, 2H), 2.20 (br s, 2H), in agreement with reference [15].

^{13}C-NMR ($CDCl_3$): δ 1.00 (CH_2), 14.63 (2CH), 26.77 (CH_2), 29.78 ($2CH_2$), 35.65 (2CH).

MS (EI) m/z (relative intensity): 108 (M^+), 93 (20), 79 (100), 66 (59), 54 (45).

Anal calc for C_8H_{12}: C, 89.93; H, 11.18. Found: C, 89.72; H, 11.22.

■ endo-*Tricylo[3.2.1.$0^{2,4}$]octane [22389-16-8]*

^{13}C-NMR ($CDCl_3$): δ 17.7 (CH_2), 23.1 (2CH), 26.8 ($2CH_2$), 36.6 (2CH), 53.5 (CH_2) in agreement with reference [15].

■ trans-*1,2-Diphenylcyclopropane [1138-47-2]*

Prepared from *trans*-stilbene.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 1.45 (m, 2H), 2.18 (m, 2H), 7.05–7.32 (m, 10H) in agreement with reference [13].

^{13}C-NMR ($CDCl_3$): δ 18.19 (CH_2), 28.00 (2CH), 125.50 (2CH), 125.75 (2CH), 128.37 (CH), 142.50 (C), in agreement with reference [13].

MS (EI) m/z (relative intensity): 194 (M^+, 100), 178 (34), 115 (61), 103 (26), 91 (48), 77 (21).

■ cis-*1,2-Diphenylcyclopropane [1138-48-3]*

Prepared by cyclopropanation of *cis*-stilbene.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 1.25–1.45 (m, 2H), 2.41 (dd, J_1 = 8.6 Hz, J_2 = 6.3 Hz, 2H), 6.90–7.10 (m, 10H), in agreement with reference [21, 39].

^{13}C-NMR ($CDCl_3$): δ 11.36 (CH_2), 24.30 (2CH), 125.73 (2CH), 127.62 (2CH), 128.95 (CH), 138.36 (C).

MS (EI) m/z (relative intensity): 194 (M^+, 100), 179 (36), 165 (10), 115 (62), 103 (24), 91 (50), 77 (28).

• *From* tert-*butyl ethyl sulfone*

■ trans-*1-Methyl-2-phenylcyclopropane [5070-01-9]*
Prepared from styrene.
^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.75 (m, 1H), 0.88 (m, 1H), 1.05 (m, 1H), 1.32 (d, J = 6.0 Hz, 3H), 1.55 (m, 1H), 7.4 (m, 5H) in agreement with references [21, 55].
^{13}C-NMR ($CDCl_3$): δ 17.59 (CH_2), 17.94 (CH), 19.05 (CH_3), 24.29 (CH), 125.41 (2CH), 128.17 (2CH), 129.21 (CH), 143.99 (C).
MS (EI) m/z (relative intensity): 132 (M^+), 117 (100), 103, 91, 78.
Anal calc for $C_{10}H_{12}$ (*trans* + *cis*): C, 90.84; H, 9.16. Found: C, 90.68; H, 9.23.

■ cis-*1-Methyl-2-phenylcyclopropane [4866-54-0]*
Prepared from styrene.
^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.70 (m, 1H), 0.90 (d, J = 6 Hz, 3H), 1.05 (m, 1H), 1.20 (m, 1H), 2.15 (m, 1H), 7.3 (m, 5H) in agreement with references [21, 55].
^{13}C-NMR ($CDCl_3$): δ 10.84 (–, cyclopropyl CH_2), 12.61 (+), 13.57 (+) (CH_3, cyclopropyl-$CHCH_3$), 21.05 (+, cyclopropyl-CHPh), 125.52 (+), 127.79 (+), 129.21 (+), 139.46 (–) (phenyl-C) in agreement with reference [16a].
MS (EI) m/z: 132 (M^+), 117 (100), 103, 91, 78.
Anal calc for $C_{10}H_{12}$ (*cis* + *trans*): C, 90.84; H, 9.16. Found: C, 90.68; H, 9.23.

■ trans-*1-Butyl-2-methylcyclopropane [38851-70-6]*
Prepared from hex-1-ene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.10–0.20 (m, 2H), 0.34–0.48 (m, 2H), 0.92 (t, J = 7.0 Hz, 3H), 1.04 (d, J = 6.0 Hz, 3H), 1.22 (m, 2H, CH_2), 1.38 (m, 4H, CH_2CH_2) in agreement with reference [56].
MS (EI) m/z (relative intensity): 112 (M^+), 97 (3), 83 (26), 70 (57), 56 (100).

■ cis-*1-Butyl-2-methylcyclopropane [38851-69-3]*
Prepared from hex-1-ene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ –0.32 (q br, J = 4.5 Hz, 1H), 0.58–0.82 (m, 3H), 0.94 (t, J = 7.0 Hz, 3H), 1.05 (d, J = 6.0 Hz, 3H), 1.20–1.45 (m, 6H) in agreement with reference [56].
MS (EI) m/z: 112 (M^+), 97, 83, 70, 56.

■ trans-*1-Methyl-2-octylcyclopropane [77422-53-8]*
Prepared from dec-1-ene.
^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.08–0.18 (m, 2H), 0.25–0.48 (m, 2H), 0.92 (t, J = 7.0 Hz, 3H), 1.01 (d, J = 5.7 Hz, 3H), 1.12–1.45 (m, 14H) in agreement with reference [16a].
^{13}C-NMR ($CDCl_3$): δ 12.63, 12.86, 14.09, 15.68, 19.04, 19.92, 22.69, 29.37, 29.68, 30.18, 31.93, 34.28 in agreement with reference [16a].
MS (EI) m/z (relative intensity): 168 (M^+), 111 (6), 97 (25), 83 (41), 69 (74), 55 (100).
Anal calc for $C_{12}H_{24}$ (*trans* + *cis*): C, 85.62; H, 14.38. Found C, 85.56; H, 14.42.

■ cis-*1-Methyl-2-octylcyclopropane [77422-52-7]*
Prepared from dec-1-ene.
^{1}H-NMR ($CDCl_3$, 250 MHz): δ –0.35 (m, 1H), 0.58–0.80 (m, 3H), 0.90 (t, J = 7.0 Hz, 3H), 1.02 (d, J = 6.0 Hz, 3H), 1.15–1.45 (m, 14H), in agreement with reference [16a].
^{13}C-NMR ($CDCl_3$): δ 9.30, 11.94, 13.20, 14.09, 15.68, 22.69, 28.47, 29.37, 29.52, 30.18, 31.93, in agreement with reference [16a].
MS (EI) m/z (relative intensity): 168 (M^+), 111 (12), 97 (46), 83 (63), 69 (84), 55 (100).
Anal calc for $C_{12}H_{24}$ (*trans* + *cis*): C, 85.62; H, 14.38. Found: C, 85.56; H, 14.42.

■ trans-*1-Decyl-2-methylcyclopropane [98678-68-3]*
Prepared from dodec-1-ene.
^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.05–0.17 (m, 2H), 0.22–0.46 (m, 2H), 0.90 (t, J = 6.9 Hz, 3H), 1.0 (d, J = 5.6 Hz, 3H), 1.10–1.48(m, 18H, $9CH_2$).
MS (EI) m/z: 196 (M^+), 125, 111, 97, 83, 69, 55 (100).

■ cis-*1-Decyl-2-methylcyclopropane [98678-67-2]*
Prepared from dodec-1-ene.
^{1}H-NMR ($CDCl_3$, 250 MHz): δ –0.30 (m, 1H), 0.60–0.81 (m, 3H), 0.90 (t, J = 6.9 Hz, 3H), 1.02 (d, J = 5.8 Hz, 3H), 1.2–1.45 (m, 18H).
MS (EI) m/z: 196 (M^+), 125, 111, 97, 83, 69, 55 (100).

■ trans-*1,2-Dibutyl-3-methylcyclopropane [98043-22-2]*
Prepared from *trans*-dec-5-ene with *tert*-butyl ethyl sulfone, or from *trans*-hept-2-ene or *cis*-hept-2-ene with *tert*-butyl pentyl sulfone.
^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.00 (m, 1H), 0.25–0.50 (m, 2H), 0.85–0.95 (m, 6H), 1.0 (d, J = 6.0 Hz, 3H), 1.05–1.42 (m, 12H, CH_2) in agreement with reference [16a].
^{13}C-NMR ($CDCl_3$): δ 12.96, 14.10, 16.79, 22.49, 22.64, 23.16, 26.32, 27.89, 31.89, 32.42, 34.03 in agreement with reference [16a].
MS (EI) m/z (relative intensity): 168 (M^+), 126 (8), 111 (10), 98 (17), 84 (22), 69 (100), 55 (73).
Anal calc for $C_{12}H_{24}$: C, 85.62; H, 14.38. Found: C, 85.41; H, 14.53.

■ exo-*9-Methylbicyclo[6.1.0]nonane [62929-24-2]*
Prepared from *cis*-cyclooctene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.11 (m, 1H), 0.28–0.36 (m, 2H), 0.88–1.00 (m, 2H) 1.05 (d, J = 6.0 Hz, 3H), 1.30–1.44 (m, 4H), 1.5–1.62 (m, 2H), 1.62–1.76 (m, 2H), 1.98–2.06 (m, 2H) in agreement with reference [16b].
^{13}C-NMR ($CDCl_3$): δ 17.55 (CH_3), 18.63 (CH), 24.16 (2CH), 26.65 ($2CH_2$), 26.69 ($2CH_2$), 29.88 ($2CH_2$), in agreement with reference [16c].
MS (EI) m/z (relative intensity): 138 (M^+), 123 (3), 110 (27), 95 (57), 81 (100), 67 (82), 55 (76).
Anal calc for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 86.68; H, 13.15.

■ endo-*9-Methylbicyclo[6.1.0]nonane [62862-04-8]*
Prepared from *cis*-cyclooctene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.45–0.60 (m, 1H), 0.70–0.80 (m, 2H), 0.92 (d, J = 6.0 Hz, 3H), 0.98–1.10 (m, 2H), 1.22–1.45 (m, 4H), 1.55–1.70 (m, 6H) in agreement with references [16a, b].
^{13}C-NMR ($CDCl_3$): δ 7.83 (q, CH_3), 11.33, (d, CH), 17.90 (d, CH), 21.55 (t, CH_2), 26.77 (t, CH_2), 29.80 (t, CH_2) in agreement with reference [16a].
MS (EI) m/z: 138 (M^+), 123 , 110, 95, 81, 67, 55.

■ *3*-exo-*Methyl*-exo-*tricyclo[3.2.1.02,4]octane*
Prepared from norbornene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.41 (d br, $J_{2,3}$ = 2.5 Hz, 2H), 0.61 (d br, J_{ab} = 10.5 Hz, 1H), 0.70 (m, 1H), 0.88 (d, J = 6.0 Hz, 3H), 0.98 (d quin, J_{ab} = 10.5 Hz, J = 2 Hz, 1H), 1.23 (m, 2H), 1.42 (m, 2H), 2.21 (s br, 2H) in agreement with reference [17].
^{13}C-NMR ($CDCl_3$): δ 7.90, 16.71, 24.25, 28.70, 29.83, 36.06.
MS (EI) m/z (relative intensity): 122 (M^+), 107 (9), 93 (71), 79 (100), 68 (91).

■ *3*-endo-*Methyl*-exo-*tricyclo[3.2.1.02,4]octane*
Prepared from norbornene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.49 (m, 1H), 0.59–0.66 (m, 3H), 1.12–1.17 (m, 1H); 1.15 (d, J = 6.2 Hz, 3H) 1.23 (m, 2H), 1.43 (m, 2H), 2.35 (s br, 2H), in agreement with reference [17].
MS (EI) m/z (relative intensity): 122 (M^+), 107 (14), 93 (72), 79 (100), 68 (66).

• *From* tert-*butyl pentyl sulfone*

■ trans-*1-Butyl-2-phenylcyclopropane [33450-83-8]*
Prepared from styrene; the same compound was also obtained from hex-1-ene and *tert*-butyl or phenyl benzyl sulfone.
^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.68–1.08 (m, 6H), 1.25–1.45 (m, 6H), 1.45–1.62 (m, 1H), 6.97–7.27 (m, 5H).
^{13}C-NMR ($CDCl_3$): δ 14.10 (CH_3), 16.18 (CH_2), 20.95 (CH), 22.50 (CH_2), 23.83 (CH), 29.70 (CH_2), 34.12 (CH_2), 125.09 (CH), 125.56 (CH), 128.19 (CH), 144.15 (C).
MS (EI) m/z (relative intensity): 174 (M^+), 145 (1), 117 (65), 104 (100), 91 (53).
Anal calc for $C_{13}H_{18}$ (*trans* + *cis*): C, 89.59; H, 10.41. Found: C, 89.67; H, 10.61.

■ cis-*1-Butyl-2-phenylcyclopropane [64286-53-9]*
Prepared from styrene; the same compound was also obtained from hex-1-ene and *tert*-butyl or phenyl benzyl sulfone.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.64 (m, 1H), 0.80 (t, J = 7.0 Hz, 3H), 0.85–1.0 (m, 2H), 1.01–1.35 (m, 6H), 2.10 (m, 1H), 7.15–7.27 (m, 5H), in agreement with reference [55].
^{13}C-NMR ($CDCl_3$): δ 9.63 (CH_2), 14.11 (CH_3), 19.08 (CH), 22.41 (CH_2), 23.22 (CH), 28.11 (CH_2), 31.62 (CH_2), 125.44 (CH), 127.73 (CH), 129.0 (CH), 139.0 (C).
MS (EI) m/z (relative intensity): 174 (M^+), 145 (1), 128 (12), 117 (74), 104 (100), 91 (35), in agreement with reference [55].
Anal calc for $C_{13}H_{18}$ (*cis* + *trans*): C, 89.59; H, 10.41. Found: C, 89.67; H, 10.61.

■ trans-*1,2-Dibutylcyclopropane [72149-16-7]*
Prepared from hex-1-ene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.16–0.22 (m, 2H), 0.36–0.50 (m, 2H), 0.90 (t, J = 7.0 Hz, 6H), 1.12–1.24 (m, 2H), 1.24–1.34 (m, 2H), 1.34–1.45 (m, 8H) ($6CH_2$), in agreement with reference [13].
^{13}C-NMR ($CDCl_3$): δ 11.75 (+, CH_2), 14.14 (–, $2CH_3$), 18.76 (–, CH), 22.72 (+), 31.95 (+), 34.08 (+), in agreement with reference [13].
MS (EI) m/z (relative intensity): 154 (M^+), 125 (2), 111 (7), 97 (27), 83 (33), 69 (71), 55 (100).
Anal calc for $C_{11}H_{22}$ (*trans* + *cis*): C, 85.62; H, 14.38. Found: C, 85.49; H, 14.46.

■ cis-*1,2-Dibutylcyclopropane [72149-17-8]*
Prepared from hex-1-ene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ −0.34 to −0.28 (m 1H), 0.58–0.76 (m, 3H), 0.94 (t, J = 7.0 Hz, 6H), 1.16–1.25 (m, 2H), 1.25–1.50 (m, 10H), in agreement with reference [13].
^{13}C-NMR ($CDCl_3$): δ 10.90 (+, CH_2), 14.14 (–, $2CH_3$), 15.74 (–, CH), 22.59 (+), 28.42 (+), 32.49 (+), in agreement with reference [13].
MS (EI) m/z (relative intensity): 154 (M^+), 125 (1), 111 (8), 97 (32), 83 (39), 69 (76), 55 (100).
Anal calc for $C_{11}H_{22}$ (*cis* + *trans*) C, 85.62; H, 14.38. Found: C, 85.49; H, 14.46.

■ trans-*1-Butyl-2-hexylcyclopropane*
Prepared from oct-1-ene.
^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.10–0.20 (m, 2H), 0.30–0.47 (m, 2H), 0.89 (t, J = 7.0 Hz, 6H), 1.05–1.44 (m, 16H).
^{13}C-NMR ($CDCl_3$): δ 11.75 (+, CH_2), 14.14 (–, $2CH_3$), 18.76 (–, CH), 22.70 (+), 29.66 (+), 30.20 (+), 31.93 (+), 31.97 (+), 34.06 (+), 34.38 (+).
MS (EI) m/z (relative intensity): 182 (M^+), 154 (1), 111 (6), 97 (21), 83 (48), 69 (100), 55 (94).
High resolution mass m/z for $C_{13}H_{26}$: calc 182.2034; found 182.2034.
Anal calc for $C_{13}H_{26}$ (*trans* + *cis*): C, 85.62; H, 14.38. Found: C, 85.65; H, 14.51.

■ cis-*1-Butyl-2-hexylcyclopropane*
Prepared from oct-1-ene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ −0.38 to −0.30 (m, 1H), 0.48–0.72 (m, 3H), 0.88–0.98 (m, 6H), 1.02–1.50 (m, 16H).
^{13}C-NMR ($CDCl_3$): δ 10.90 (+, CH_2), 14.14 (–, $2CH_3$), 15.74 (–), 15.77 (–, CH), 22.57 (+), 28.40 (+), 28.73 (+) 29.21 (+), 29.37 (+), 31.97 (+), 32.47 (+).
MS (EI) m/z (relative intensity): 182 (M^+), 154 (1), 111 (7), 97 (21), 83 (47), 69 (87), 55 (100).
High resolution mass m/z for $C_{13}H_{26}$: calc 182.2034; found 182.2034.
Anal calc for $C_{13}H_{26}$ (*cis* + *trans*): C, 85.62; H, 14.38. Found: C, 85.65; H, 14.51.

■ *1,2*-trans-*Diphenyl-3-butylcyclopropane*
Prepared from *trans*-stilbene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.78 (t, J = 7.0 Hz, 3H), 1.02–1.15 (m, 1H), 1.16–1.50 (m, 6H), 2.17 (t, J = 5.5 Hz, 1H), 2.46 (dd, J_1 = 9.0 Hz, J_2 = 5.5 Hz, 1H).
^{13}C-NMR ($CDCl_3$): δ 14.00 (–, CH_3), 22.41 (+, CH_2), 28.14 (+, CH_2), 28.63 (–, CH), 30.17 (–, CH), 31.56 (+, CH_2), 32.24 (–, CH), 125.51 (–), 125.85 (–), 126.12 (–), 127.96 (–), 128.33 (–), 128.95 (–), 138.74 (+), 143.11 (+).
MS (EI) m/z (relative intensity): 250 (M^+), 193 (62), 178 (13), 115 (100), 91 (83).
High resolution mass m/z for $C_{19}H_{22}$: calc 250.17215; found 250.1724.

■ exo-*9-Butylbicyclo[6.1.0]nonane*
Prepared from *cis*-cyclooctene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.07 (m, 1H), 0.34 (m, 2H), 0.90 (t, J = 7.0 Hz, 3H), 0.87–1.02 (m, 2H), 1.22–1.30 (m, 2H), 1.30–1.45 (m, 8H), 1.48–1.62 (m, 2H), 1.62–1.78 (m, 2H), 2.01 (m, 2H).
^{13}C-NMR ($CDCl_3$): δ 14.20 (–, CH_3), 22.50 (+, CH_2), 23.04 (–), 23.84 (–) (C-1, C-8, C-9), 26.66 (+), 26.97 (+), 29.92 (+) (C-2, C-7; C-3, C-6; C-4, C-5), 32.02 (+), 33.71 (+).
MS (EI) m/z (relative intensity): 180 (M^+, 10), 152 (3), 123 (13), 109 (16), 95 (45), 81 (100), 67 (88), 55 (60).
Anal calc for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.58; H, 13.50.

■ endo-*9-Butylbicyclo[6.1.0]nonane*
Prepared from *cis*-cyclooctene.
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.58–0.74 (3H, m), 0.9–1.02 (m, 2H), 0.95 (t, J = 7.0 Hz, CH_3), 1.05–1.15 (m, 2H), 1.3–1.8 (m, 14H).
MS (EI) m/z (relative intensity): 180 (M^+), 152 (2), 123 (4), 109 (8), 95 (59), 81 (79), 67 (100), 55 (67).

High resolution mass m/z for $C_{13}H_{24}$: calc 180.1878; found 180.1878.

■ *3*-exo-*Butyl*-exo-*tricyclo[3.2.1.02,4]octane*
Prepared from norbornene.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.42 (d br, J = 2.4 Hz, 2H), 0.61 (d br, J = 10.5 Hz, 1H), 0.66 (m, 1H), 0.91 (t, J = 7.0 Hz, 3H), 0.97 (d quin, J = 10.5 Hz, J = 2.0 Hz, 1H), 1.05–1.14 (m, 2H), 1.20–1.28 (m, 2H), 1.28–1.38 (m, 4H), 1.40–1.46 (m, 2H), 2.25 (s br, 2H).

^{13}C-NMR ($CDCl_3$): δ 13.91 (+), 14.14 (+), 22.62 (–, CH_2), 22.87 (+, CH), 28.66 (–, CH_2), 29.79 (–, CH_2), 31.70 (–, CH_2), 36.01 (+, CH).

MS (EI) m/z (relative intensity): 164 (M^+, 14), 149 (2), 135 (12), 122 (36), 110 (46), 107 (26), 93 (55), 91 (60), 80 (64), 79 (100), 67 (43), 57 (38).

High resolution mass m/z for $C_{12}H_{20}$: calc 164.15650; found 164.1569.

■ *3*-endo-*Butyl*-exo-*tricyclo[3.2.1.02,4]octane*
Prepared from norbornene.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.42 (m, 1H), 0.67 (d br, J = 10.5 Hz, 1H), 0.71 (d br, J = 8.0 Hz, 2H), 0.94 (t, J = 7.0 Hz, 3H), 1.15 (d quin, J = 10.5 Hz, J = 2.0 Hz, 1H), 1.22–1.30 (m, 2H), 1.30–1.42 (m, 4H), 1.42–1.50 (m, 2H), 1.5–1.58 (m, 2H), 2.39 (s br, 2H).

MS (EI) m/z (relative intensity): 164 (M^+, 7), 149 (1), 135 (16), 122 (34), 110 (25), 107 (25), 93 (46), 91 (28), 80 (57), 79 (100), 67 (34), 57 (14).

High resolution mass m/z for $C_{12}H_{20}$: calc 164.15650; found 164.1560.

■ trans-*1-Butyl-2-(2-methylprop-1-enyl)cyclopropane*
Prepared from 4-methylpenta-1,3-diene.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.42 (m, 1H), 0.62 (m, 1H), 0.8–0.96 (m, 4H), 1.18 (m, 1H), 1.32 (m, 6H), 1.70 (m, 6H), 4.58 (m, 1H).

^{13}C-NMR ($CDCl_3$): δ (*trans* + *cis*) 13.36, 13.79, 14.08, 14.61, 18.02, 18.07, 20.55, 22.46, 22.52, 25.50, 25.71, 29.09, 31.65, 31.95, 33.71, 123.99, 128.39, 129.65, 132.16.

MS (EI) m/z (relative intensity): 152 (M^+), 109 (9), 96 (100), 82 (74), 67 (95), 55 (51).

High resolution mass m/z for $C_{11}H_{20}$: calc 152.1565; found 152.1563.

■ cis-*1-Butyl-2-(2-methylprop-1-enyl)cyclopropane*
Prepared from 4-methylpenta-1,3-diene.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.01 (m, 1H), 0.42 (m, 1H), 0.82–0.98 (m, 4H), 1.3 (m, 6H), 1.42 (m, 1H), 1.7 (m, 6H), 4.82 (m, 1H).

^{13}C-NMR ($CDCl_3$) (*cis* + *trans*): δ 13.36, 13.79, 14.08, 14.61, 18.02, 18.07, 20.55, 22.46, 22.52, 25.50, 25.71, 29.09, 31.65, 31.95, 33.71, 123.99, 128.39, 129.65, 132.16.

MS (EI) m/z (relative intensity) 152 (M^+, 24), 109 (10), 96 (100), 82 (74), 67 (92), 55 (40).

High resolution mass m/z for $C_{11}H_{20}$: calc 152.1565; found 152.1563.

• *From* tert-*butyl dodecyl sulfone*

■ trans-*1-Butyl-2-undecylcyclopropane*
Prepared from hex-1-ene.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.08–0.20 (m, 2H), 0.27–0.42 (m, 2H), 0.88 (m, 6H), 1.00–1.45 (m, 26H).

MS (EI) m/z (relative intensity): 252 (M^+), 224 (0.5), 125 (5), 111 (19), 97 (43), 83 (93), 69 (70), 55 (100).

■ cis-*1-Butyl-2-undecylcyclopropane*
Prepared from hex-1-ene.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ –0.35 to –0.25 (m, 1H), 0.55–0.72 (m, 3H), 0.89 (m, 6H), 1.10–1.50 (m, 26H).

MS (EI) m/z (relative intensity): 252 (M^+), 224 (0.5), 125 (7), 111 (20), 97 (46), 83 (51), 69 (72), 55 (100).

• *From* tert-*butyl isopropyl or diisopropyl sulfone*

■ *1,1-Dimethyl-2-phenylcyclopropane [7653-94-3]*
Prepared from styrene.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.84 (m, 2H), 0.86 (s, 3H), 1.30 (s, 3H), 1.95 (dd, J = 8.4 Hz, J = 6.0 Hz, 1H), 7.2–7.35 (m, 5H), in agreement with references [19, 21].

^{13}C-NMR ($CDCl_3$): δ 18.30 (–), 18.92 (–), 20.32 (+, CH_3), 27.44 (+, CH_3), 29.75 (+, CH), 125.45 (+), 127.82 (+), 128.89 (+), 140.26 (–).

MS (EI) m/z (relative intensity) 146 (M^+, 34), 131 (100), 115 (15), 103 (11), 91 (52), 77(12).

Anal calc for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.28; H, 9.74.

■ *1,1-Dimethyl-2-octylcyclopropane [83096-25-7]*
Prepared from dec-1-ene.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ –0.18 (t, J = 4.5 Hz, 1H), 0.32 (dd, J = 8.6 Hz, J = 4.6 Hz, 1H), 0.45 (m, 1H), 0.88 (t, J = 7.0 Hz, 3H), 1.0 (s, 3H), 1.02 (s, 3H), 1.20–1.40 (m, 14H).

MS (EI) m/z: 182 (M^+), 125, 97, 83, 69 (100).

■ trans-*1,1,2-Trimethyl-3-phenylcyclopropane [5381-42-0]*
Prepared from *trans*-β-methylstyrene.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.76 (s, 3H), 1.05 (m, 1H), 1.16 (s, 3H), 1.18 (d, J = 6.5 Hz, 3H), 1.45 (d, J = 5.5 Hz, 1H), 7.12–7.32 (m, 5H), in agreement with reference [21].

^{13}C-NMR ($CDCl_3$): δ 13.69 (–), 21.40 (–), 22.02 (–), 23.03 (–) 36.97 (–) (3 CH_3, C-2, C-3), 22.90 (+, C-1), 125.28 (–), 127.77 (–), 128.70 (–), 140.69 (+).

MS (EI) m/z (relative intensity): 160 (M^+, 51), 145 (92), 129 (9), 117 (27), 105 (11), 91 (100), 77 (22).

■ *9,9-Dimethylbicyclo[6.1.0]nonane*
Prepared from *cis*-cyclooctene.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.32 (m, 2H), 0.94 (s, 3H), 1.02 (s, H), 0.98–1.08 (m, 2H), 1.38 (m, 4H), 1.52–1.82 (m, 6H).

^{13}C-NMR ($CDCl_3$): δ 15.03 (+), 26.57 (+), 29.21 (+),16.41 (–, C), 22.39 (–), 26.57 (–), 29.71 (–).

MS (EI) m/z (relative intensity): 152 (M^+, 9), 137 (4), 124 (19), 109 (26), 94 (44), 81 (61), 67 (100), 55 (76).

High resolution mass m/z for $C_{11}H_{20}$: calc 152.1565; found 152.1566.

• *From* tert-*butyl benzyl sulfone*
1-Butyl-2-phenylcyclopropane and 1,2-diphenylcyclopropane prepared from hex-1-ene and styrene respectively were described above.

■ exo-*7-Phenylbicyclo[4.1.0]heptane [10503-37-4]*
Prepared from cyclohexene.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 1.12–1.36 (m, 6H), 1.50 (t, J = 4.8 Hz, 1H), 1.70 (m, 2H), 1.90 (m, 2H), 6.92 (m, 2H), 7.05 (m, 1H), 7.18 (m, 2H), in agreement with reference [57].

^{13}C-NMR ($CDCl_3$): δ 21.37 (–, $2CH_2$), 22.72 (+, CH), 23.57 (–, $2CH_2$), 28.55 (+, CH), 124.81 (+), 125.00 (+), 130.14 (+), 144.65 (–).

MS (EI) m/z (relative intensity): 172 (M^+, 6), 128 (22), 115 (68), 104 (100), 91 (50), 81 (44), 65 (11).

■ endo-*7-Phenyl bicyclo[4.1.0]heptane [10503-36-3]*
Prepared from cyclohexene.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.58–0.82 (m, 2H), 0.95–1.20 (m, 2H), 1.20–1.40 (m, 2H), 1.55–1.80 (m, 2H), 1.80–2.05 (m, 3H), 7.28 (m, 5), in agreement with references [57, 58].

^{13}C-NMR ($CDCl_3$): δ 12.60 (+, CH), 20.18 (–, $2CH_2$), 21.68 (–, $2CH_2$), 22.06 (+, CH), 125.59 (+), 128. 06 (+), 131.17 (+), 138.49 (–).

MS (EI) m/z (relative intensity): 172 (M^+, 6), 128 (38), 115 (100), 104 (90), 91 (76), 81 (91), 77 (20).

• *From* tert-*butyl prenyl sulfone*

■ trans-*1-(2-Methylprop-1-enyl)-2-phenylcyclopropane [89486-57-7]*
Prepared from styrene.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.9–1.00 (m, 1H), 1.12–1.18 (m, 1H), 1.65 (m, 1H), 1.7 (m, 6H), 1.85 (m, 1H), 4.8 (m, 1H), 7.25 (m, 5H), in agreement with reference [19].

MS (EI) m/z (relative intensity): 172 (M^+, 37), 157 (42), 142 (22), 129 (100), 115 (25), 91 (47), 77 (34).

■ cis-*1-(2-Methylprop-1-enyl)-2-phenylcyclopropane [89486-56-6]*
Prepared from styrene.

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.75–0.90 (m, 1H), 1.15–1.25 (m, 1H), 1.55–1.75 (m, 6H), 1.90 (m, 1H), 2.20–2.35 (m, 1H), 4.55 (m, 1H), 7.20 (m, 5H), in agreement with reference [19].

MS (EI) m/z (relative intensity): 172 (M^+, 32), 157 (41), 142 (26), 129 (100), 115 (27), 91 (39), 77 (22).

• *Competitive reactions for the Hammett correlation*
The general experimental procedure was followed. An equimolar mixture of styrene and *para*-substituted styrene was used. The olefin/methyl sulfone ratio was 2.4:1. The reaction mixture was refluxed for a shorter period, typically 45 min. The molar ratio of *para*-substituted phenylcyclopropane and phenylcyclopropane was used as a measurement of the ratio of the rate constants: *p*-methoxystyrene: k_{MeO}/k_H = 0.30; *p*-methylstyrene: k_{Me}/k_H = 0.46; *p*-fluorostyrene: k_F/k_H = 1.24; *p*-chlorostyrene: k_{Cl}/k_H = 2.69.

■ *(4-Methoxyphenyl)cyclopropane [4030-17-5]*

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.72 (m, 2H), 1.0 (m, 2H), 1.90 (m, 1H), 3.70 (s, 3H), 7.0–7.35 (m, 4H), in agreement with reference [59].

MS (EI) m/z (relative intensity): 148 (M^+, 100), 147 (M^+ – 1, 75), 133 (23), 121 (23), 117 (38), 105 (18), 91 (17), 77 (39), 65 (13).

■ *(4-Methylphenyl)cyclopropane [6921-43-3]*

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.69 (m, 2H), 0.96 (m, 2H), 1.88 (m, 1H), 2.32 (s, 3H), 7.0–7.3 (m, 4H), in agreement with reference [59].

MS (EI) m/z (relative intensity): 132 (M^+, 53), 117 (M^+ – CH_3, 100), 115 (39), 91 (24), 77 (15), 65 (16).

■ *(4-Fluorophenyl)cyclopropane [18511-60-9]*

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.70 (m, 2H), 0.97 (m, 2H), 1.90 (m, 1H), 7.0–7.35 (m, 4H), in agreement with reference [59].

MS (EI) m/z (relative intensity): 136 (M^+, 73), 135 (M^+ – 1, 100), 115 (27), 109 (38), 83 (12), 75 (10).

■ *(4-Chlorophenyl)cyclopropane [1798-84-1]*

^{1}H-NMR ($CDCl_3$, 250 MHz): δ 0.70 (m, 2H), 0.98 (m, 2H), 1.90 (m, 1H), 7.1–7.4 (m, 4H), in agreement with reference [59].

MS (EI) m/z (relative intensity): 152 (M^+, 43), 125 (11), 117 (M^+ – Cl, 100), 115 (58), 91 (12), 75 (9), 57 (15).

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Temperature effect on overloaded elution properties of cyclodextrins in reversed-phase chromatography

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Summary — The temperature effects on the retention properties of native cyclodextrins (CDs) are studied under overloaded reversed-phase liquid chromatographic conditions. For all native CDs a strong temperature dependence is observed. The analysis of adsorption isotherms confirms a different retention mechanism for α-CD compared to that for the larger β-, γ-CDs. The strong variations in the determined isotherm parameters due to the temperature variations are discussed in terms of the solvophobic theory and structural organization. Analysis of the entropy contribution to the isotherm obtained by a Van't Hoff plot suggests higher ordering when the CDs are bound to the stationary phase. Finally, the influence of the studied temperature effect on errors encountered in isotherm determination using the ECP method is analysed.

liquid chromatography / cyclodextrin / thermodynamic study / adsorption isotherm

Résumé — Effets de température sur les propriétés d'élution des cyclodextrines en chromatographie en phase inverse dans des conditions de surcharge. *Les variations du temps de rétention en chromatographie liquide en phase inverse en fonction de la température sur des cyclodextrines natives sont étudiées dans des conditions de surcharge de produit injecté. Une forte corrélation entre le temps de rétention et la température a été observée pour toutes les cyclodextrines natives. L'analyse des isothermes d'adsorption révèle que le mécanisme de la rétention de l'α-CD est différent de celui des β- et γ-CD. Les fortes variations des paramètres des isothermes en fonction de la température sont analysées dans le contexte de la théorie de solvophobicité et de l'organisation structurale des cyclodextrines à la surface de la phase. La contribution de l'entropie calculée à partir d'une courbe de Van't Hoff suggère que les cyclodextrines induisent une meilleure organisation lorsqu'elles sont liées à la phase stationnaire. L'effet des variations de température sur les erreurs d'analyse est discuté en utilisant la méthode ECP.*

chromatographie en phase liquide / cyclodextrine / étude thermodynamique / isotherme d'adsorption

Introduction

The cyclodextrins (CDs) are a class of cyclic oligosacharides, having 6, 7 or 8 (α-, β-, γ-CD) glucopyranose units linked α, 1–4. Their geometry is that of a truncated cone, with two hydrophobic faces surrounding a relatively nonpolar cavity of variable diameter (α = 5.7 Å, β = 7.8 Å, γ = 9.5 Å) [1]. The capacity of this cavity to include and transport a wide range of organic molecules has led to their application in the food, cosmetic, agrochemical sciences [2–5], and especially in the separation sciences [6–18]. They have been widely used as both stationary [6-8] and mobile phase [9–11] modifiers in GLC [12–15], electrophoresis [16–18], and HPLC [6–10].

In this paper we focus on the influence of temperature on the elution properties of native CDs (α-, β-, γ-CD), observed under overloaded conditions in reversed-phase liquid chromatographic systems. Based on the overloaded peak profiles, the adsorption isotherms were determined by the elution by characteristic points (ECP) method [19–21]. The changes in the estimated isotherm parameters due to temperature variations were studied for all native CDs in two chromatographic systems. The discussion is linked with previous investigations based on the molecular modelling of the CD–RP stationary phase interaction [22].

Experimental section

Apparatus

A chromatographic system was set up using a Varian (Walnut Creek, CA, USA) model 5000 pump, a Rheodyne

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(Cotati, CA, USA) injection device model 7125 with a 250 or 10 μL loop. Detection was performed through a refractive index detector Pye Unicam (Philips, The Netherlands) model PU4023.

The column 25 x 0.46 cm was packed with commercially available sorbent Lichrospher RP18, particle size 5 μm, pore size 100 Å (Merck, Paris, France). The temperature of mobile phase tank, column, detection device and tubing connections were kept constant (±0.5 °C) using a cryostat model WK5 from Colora Mess-Technik (Wurt, Germany).

Materials

HPLC grade methanol from Prolabo (Vitry, France), and Chromasolv acetonitrile from Riedel de Haën (Sellse, Germany) were used as the organic modifiers in the mobile phase, aqueous–organic mixtures made with freshly double-distilled water. The elution phases were filtered on a 0.45 μm membrane prior to use in a closed and saturated chamber to avoid composition modification due to evaporation. The methanol/water (8:92, v/v) mixture is noted as *System 1*, and the acetonitrile/water (2.9:97.1, v/v) is noted as *System 2*.

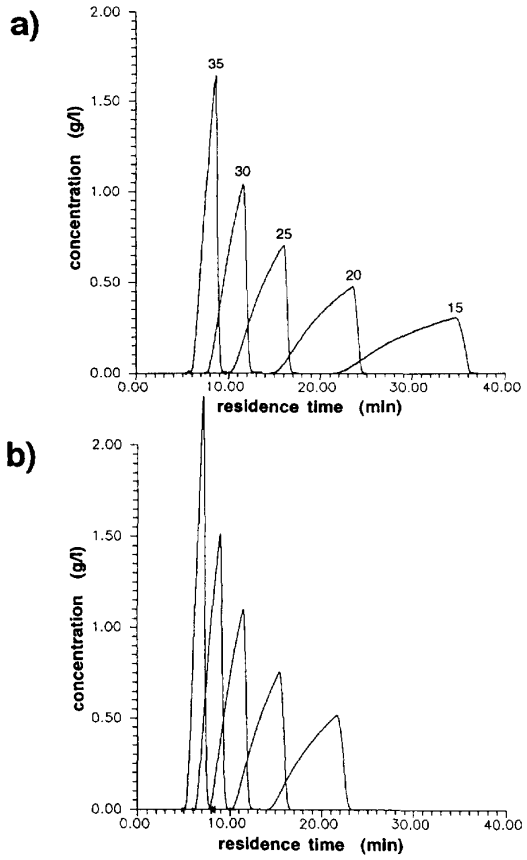

Fig 1. Chromatograms of α-CD obtained for five different temperatures: 15, 20, 25, 30, 35 °C in *System 1* (a) and *System 2* (b). Chromatographic conditions: 250 μL loop, 1 mL/min, mobile phase: methanol/water (8:92 v/v) as *System 1*, acetonitrile/water (2.9:97.1 v/v) as *System 2*, refractive index detector, 0.1 RI FS, computer data acquisition at 12 bits, and 2 Hz, ie, 200 data points per peak.

α-, β- and γ-CD were a gift from Wacker SA (Lyon, France).

Procedures

Using the 10 μL injection loop, and copper sulfate solutions (0.01 mg/mL) the void volume of the system was determined as 2.2 ± 0.1 mL using either the aqueous–organic mixtures, pure water or pure methanol. This procedure was applied systematically twice a day during the experiments. Therefore, we can assume that the void volume variation of the chromatographic system may be neglected. α-, β- and γ-CD were diluted prior to use in the mobile phase with final concentration 10 g/L. For five different temperatures, 15, 20, 25, 30, and 35 °C, each CD elution was performed at least three times. CD solutions were systematically injected at the column inlet through the 250 μL loop. Data acquisition at 100 Hz was performed with a laboratory-developed system (12 bit resolution) analogous to one described previously [23, 24], and ASCII data were transferred via RS232 protocol to either a Macintosh SI or an IBM (486)-compatible computer. File lengths were then reduced by two successive averaging smoothing operations corresponding finally to a 2 Hz acquisition, each chromatographic peak numbering at least 200 points is shown in figures 1–3. Based on this data the isotherm determination has been performed. The computer program for calculation and numerical fitting was written in Fortran.

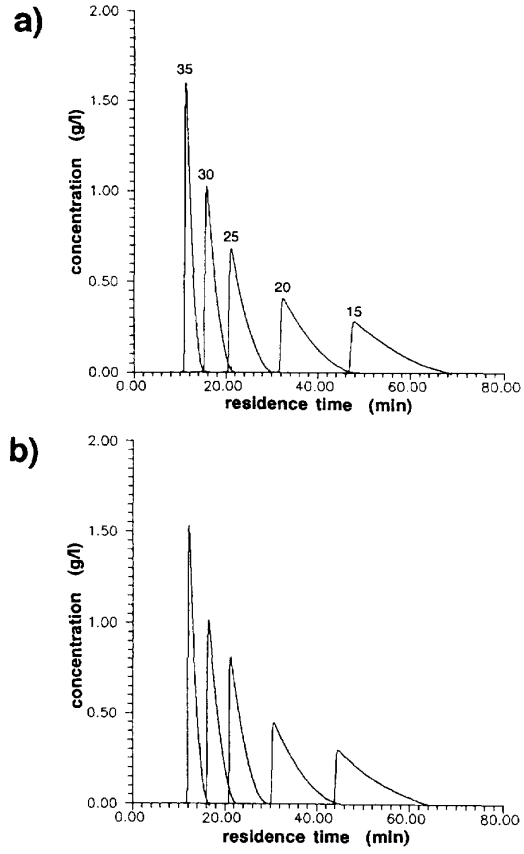

Fig 2. Chromatograms of β-CD obtained for five different temperatures: 15, 20, 25, 30, 35 °C in *System 1* (a) and *System 2* (b). Chromatographic conditions as in figure 1.

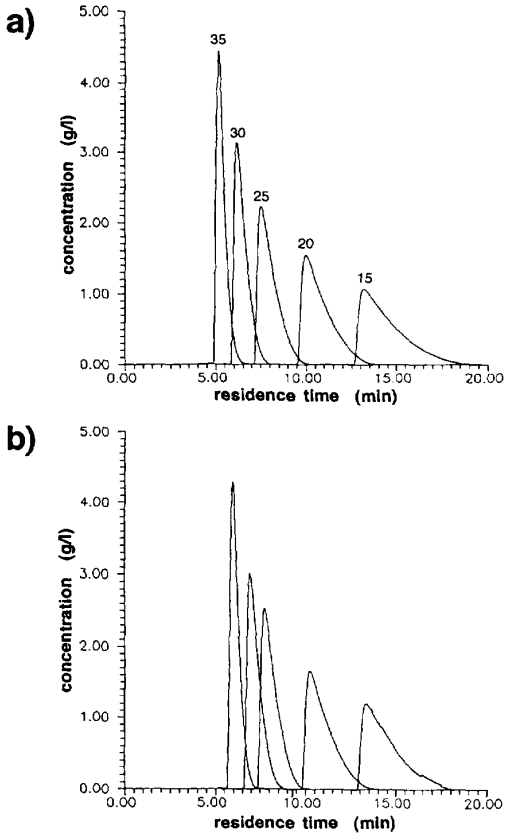

Fig 3. Chromatograms of γ-CD obtained for five different temperatures, 15, 20, 25, 30 and 35 °C, in *System 1* (a) and *System 2* (b). Chromatographic conditions as in figure 1.

Results and discussion

The objective of this paper is to study the influence of temperature on the sorption properties and resulting retention of the natural CDs in reversed-phase chromatographic systems. Starting from the experimental chromatograms obtained in the overloaded conditions, the isotherm functions were determined and their characteristics versus temperature were analysed.

CD elution in overloaded conditions

Two binary solutions of methanol/water (*System 1*) and acetonitrile/water (*System 2*) were used as a mobile phase for the experiments. The percentage of each organic modifier was chosen to produce an identical analytical retention for β-CD in 25 °C, whatever the difference in their elution strength.

The chromatograms obtained for natural α-, β- and γ-CD in both systems at five different temperatures in range 15–35 °C are presented in figures 1–3. Both systems confirm α-CD as possessing a different overloading profile modification from β- and γ-CDs, because of the concave shape of isotherms [25]. The retention of CD always increased with decreasing temperature. A more complete study of these properties will be performed by distribution isotherm analysis.

Isotherm analysis

Isotherms were determined from the points of the appropriate boundary of the detected peaks by the previously described ECP method [26–28]. Due to the different shapes of isotherms two different equations were used to fit the results obtained. Langmuir theory was used for the β- and γ-CD, assuming a monomolecular adsorbate layer [29]. For α-CD a different equation corresponding to a concave curve was used, assuming a limited miscibility of the substance in the mobile phase [30, 31]. In both cases the isotherms were characterized by a set of two parameters. The first, the common parameter for two models used, is $k(0)$ and describes the slope of the isotherm for the equilibrium concentration in the mobile phase equal to zero. Therefore, it corresponds to the capacity factor observed under analytical conditions. The second parameter, describing the capacity of appropriate phase, has different significance and notation in both cases (Q_s,Q^*). In Langmuir theory Q_s describes the capacity of the monomolecular adsorbate layer of CD in the stationary phase. In contrast, in the case of α-CD, Q^* characterizes a capacity of the mobile phase corresponding to the maximum miscibility of the cyclodextrin in that phase. The isotherm equations with the detailed discussion of their parameters were recently described [30].

All parameters were determined from the isotherm points by a recursive fitting procedure. The values coupled with the minimum fitting residual errors are reported in table I. Moreover, to show the results of the fitting procedure the isotherm data points with the appropriate fitted theoretical curves are presented in figures 4–6.

Capacity factor k*(0)*

With increasing temperature, $k(0)$ decreased. This is classical, but for CDs, large differences were observed, a factor of five in $k(0)$ is observed for a 20 °C variation.

Table I. Isotherm parameters of α-, β- and γ-CD.

Temperature (°C)	*System 1* k(O)	$Q_{(s)}$[a] *[g/L]*	*System 2* k(O)	$Q_{(s)}$[a] *[g/L]*
α-CD				
15	9.08	1.51*	5.63	2.70*
20	5.97	2.30*	3.79	3.76*
25	3.79	3.21*	2.65	5.27*
30	2.62	4.64*	1.93	6.93*
35	1.81	7.07*	1.46	10.66*
β-CD				
15	29.30	40.65	27.72	37.72
20	19.80	40.30	18.58	37.56
25	12.16	42.10	11.78	39.10
30	8.34	45.89	8.74	45.00
35	5.49	49.20	6.08	49.80
γ-CD				
15	7.12	35.40	6.98	42.72
20	4.93	38.46	4.97	43.82
25	3.33	39.56	3.50	52.48
30	2.42	43.02	2.79	54.00
35	1.77	46.94	2.16	58.00

[a] Concave isotherm shape with capacity parameter Q^*.