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5-*(ENDO)*-ISOPROPYLSULFONYL- 5-*(EXO)*-PHENYL-2-NORBORNENE : X-RAY AND MOLECULAR MECHANICS ASSESSMENT OF THE HIGH EFFICIENCY OF THIS NEW RADICAL CLOCK.

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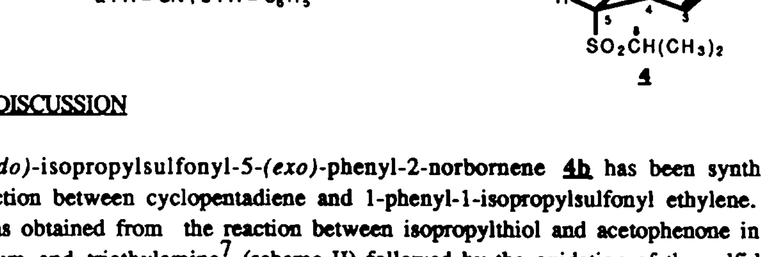
Abstract.- The synthesis of 5-*(endo)*-(1'-chloro-1'-methylethyl)sulfonyl-5-*(exo)*-phenyl- 2-norbornene a new highly efficient radical clock is described. The rate of the intramolecular radical cyclization (addition of a C-centered α-sulfonyl radical on a double bond) is presently one of the fastest ($10^9 s^{-1} l^{-1}$). In order to explain this interesting value, force field calculations (MM2 method) and X ray analysis were performed for the title compound and for the corresponding 5-*(exo)*-cyano compound. The enhancement of the efficiency in the case of the former is mainly due to the effect of the *(exo)*-phenyl which pushes the whole *endo* substituent toward the double bond of the norbornenyl group.

The use of radical clocks is a very convenient approach to check for the presence of radical intermediates during organic reactions.[1] In particular, alkyl halide precursors of cyclisable radicals have been successfully applied to mechanistic studies.[2,3] The efficiency of this kind of radical clocks is governed by their cyclization rate (i.e., intramolecular rate of addition of the radical on a double bond). During a study [4a]aiming at the trapping of probably highly elusive radical /anion -radical pair[4b],we have been led to design free radical clocks [1] of ever increasing efficiency. Following Ashby's norbornyl kind of free radical clock[3] we have recently synthesized[5] 5-*(endo)*-(1'-chloro-1'-methylethyl)sulfonyl-5-*(exo)*-cyano-2-norbornene (**1a**) which leads to a cyclization rate near $10^8 s^{-1}$ for the radical **2a** (Scheme I). In order to enhance this interesting value, we changed the cyano group to a substituent which could, by stereopopulation control [6], induce conformations in the radical even more favourable for addition on the C_2-C_3 double bond. We describe in the present work the synthesis of a new radical clock (5-(*endo*)-(1'-chloro-1'-methylethyl)sulfonyl-5-(*exo*)-phenyl- 2-norbornene) (**1b**), the evaluation of the corresponding intramolecular cyclization rate, and explain the high efficiency observed using molecular mechanics calculation.

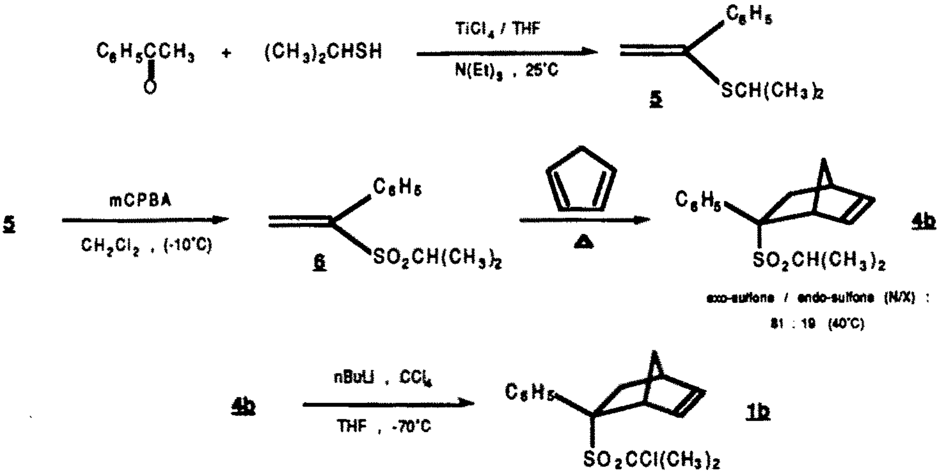
Scheme I



RESULTS AND DISCUSSION

5-*(endo)*-isopropylsulfonyl-5-*(exo)*-phenyl-2-norbornene **4b** has been synthesized from the Diels-Alder reaction between cyclopentadiene and 1-phenyl-1-isopropylsulfonyl ethylene. The dienophilic compound **5** was obtained from the reaction between isopropylthiol and acetophenone in the presence of tetrachlorotitanium and triethylamine[7] (scheme II) followed by the oxidation of the sulfide to the sulfone. The direct Diels-Alder reaction between **5** and cyclopentadiene (in spite of the supposed capto-dative nature of **5**),[8,9] as well as its catalytic adaptations with Lewis acids (ZnI_2 or $SnCl_4$)[10] or with the radical-cation (Ar_3NSbCl_6)[11]were unsuccessful; these substrates under Diels Alder conditions mainly yield polymerisation.[12]

Scheme II



The pure *endo*-sulfone **4b** (10% yield) is obtained from silica-gel chromatography followed by crystallization in a hexane-diethylether mixture. The structure has been confirmed by X-Ray determination (figure 1).The sulfone **4b** treated with n-butyllithium and hexachloroethane at -70°C in tetrahydrofuran [13] yields 88% of the halogenated compound **1b** .

The radical **2b** has been generated by reducing **1b** with tributyltinhydride[14] (scheme I). We used increasing quantities of Bu_3SnH, and the ratio between the normal reduced sulfone **4b** and the cyclized one **3b** provided an estimation of the cyclization rate for the radical **2b**[15], the relation being : $k_{cycl} = k_H[Bu_3SnH]_0$ [**3b**] / [**4b**]. $[Bu_3SnH]_0$ is the initial concentration in reductant and k_H is the rate constant for the abstraction of H' from tributyltinhydride by the C-centered α-sulfonyl radical. Using for this last value 1.87 10^6 $M^{-1}s^{-1}$ (at 300 K) measured by K.U. Ingold and coworkers[16] for a tertiary radical corrected taking into account the Arrhenius parameters of the reaction[16] for our experimental temperature c.a. 80°C and we obtained $k_H = 6.3\ 10^6\ M^{-1}s^{-1}$. The experimental results obtained lead for the rate constant of the cyclisation reaction 1.1 $10^9 s^{-1}l^{-1}$ (at 353K). In the case of the 5-*(exo)*-cyano derivative the value calculated with the corrected k_H is 2.0 $10^8 s^{-1}l^{-1}$. The high efficiency of this kind of radical clock makes them effective to study the possible intervention of radical species during the reaction of α-sulfonyl carbanions[4a,5] or the reduction of α-halosulfones[4a] but the accessibility of **4b** is greatly affected by the low *endo*-sulfone isomer ratio obtained during the Diels Alder step.

These results lead to the question:*why the substitution of a cyano group by a phenyl group in the 5-exo position induces an increase in the cyclization rate of the intermediate radical* **2** ?

In order to explain the enhancement of this rate in relation to the corresponding 5-cyano derivative, we performed X ray analysis and force field calculations[17] on both compounds.

X-ray structures show that in the crystal, the isopropylsulfonyl group is placed in a favourable conformation to undergo cyclization for **4a** (figure 2) but not for the compound **4b** (figure 1). This conformational preference could, however, originate from crystal lattice interactions.

For the studied radicals, MM2 calculations[18a] were performed on the parent H compounds. It would be more exact to perform these calculations on the C-centered radicals using the required parameters recently published by Allinger for alkyl radicals [18b]. These parameters are attributed to a planar like C-radical with 120° bond angles. In the case of α- sulfonyl-C-centered radicals, although e.s.r. experiments tend to show a planarity at the radical center[19], MNDO calculations performed on dimethyl sulfone found a minimal energy for a C-centered radical more pyramidal like (bond angles near 113°). Moreover, features of this radical are capable of modifications depending on the fixed substituents. We have verified that the use of Allinger's radical parameters [18b] (calculation performed on **4b**) tend to minimize the steric energy in the more constrained conformation by about 3 kcal, minimizing as much the calculated rotational barrier around the C-S bond. This variation should be relatively constant for both compounds studied and does not modify the following discussion. Note that recently D.C. Spellmeyer and K.N. Houk published a force-field model for intramolecular radical additions.[20] Rotations Θ around the 5-*(endo)* C_5-S bond have been simulated in order to obtain the most stable conformation (Θ=0). The ΔE_s values correspond to the calculated difference in energy between the most stable conformer and the conformer best spatially suited for obtaining the intramolecular cyclization i.e. corresponding to a

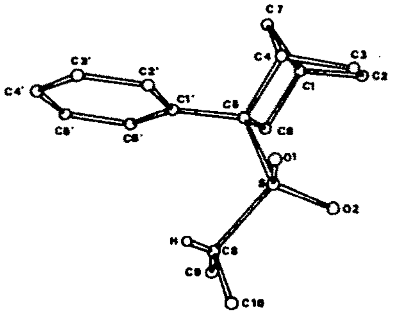


Figure 1 : X-ray crystallographic stucture of compound **4b**

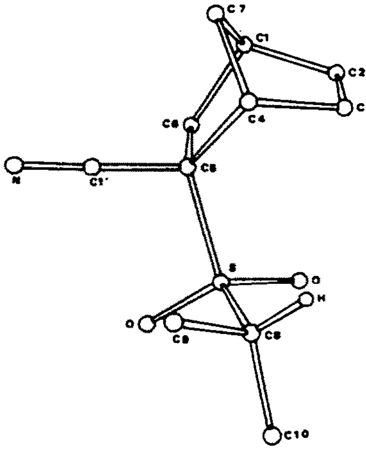


Figure 2 : X-ray crystallographic stucture of compound **4a**

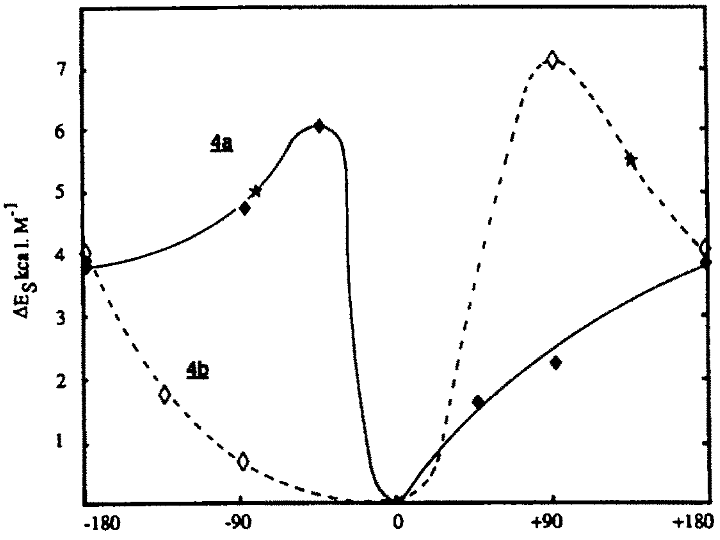


Figure 3. Steric energy (ΔE_s, kcal. mole^{-1}, from MM2 calculations) of the norbornenyl derivatives **4a** and **4b** as a function of the rotation angle Θ about the 5-*(endo)* C_5-S bond. ($\Delta E_s = E_s(\Theta) - E_s(0)$, Θ corresponding in each case to the stablest conformer displayed in figure 4). The points corresponding to the minimal distance between the reactive sites are reported as ★.

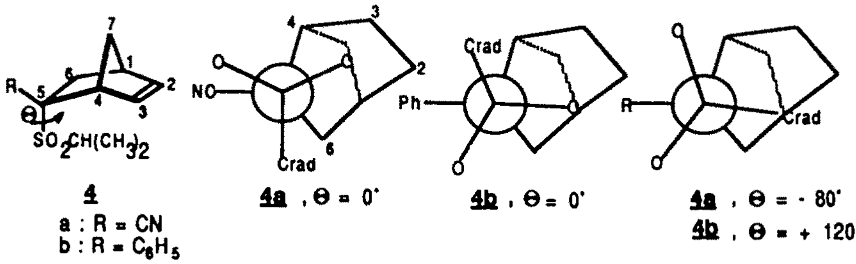


Figure 4. Rotations around the *endo* C_5-S bond : Newmann's representations of the conformations corresponding to the minimum steric energy ($\Theta = 0°$), and to the minimum distance between the reactive sites Crad and C_3 ($\Theta = -80°$ and $\Theta = +120°$ respectively for **4a** and **4b**).

minimal distance between the reactive sites (carbon atom C_8 bearing the radical (C_{rad}) and nearest carbon atom of the double bond C_3 (figure 4)).The variations of ΔE_s displayed in figure 3 correspond to changes in energy when Θ is modified from zero (stablest conformer) to +180° and -180°. Crystallographic bond lengths and valence angles of compounds **4a** and **4b** have been used to perform the calculations (tables 1and 2).

Conformational calculations performed with the MM2 method show that the rotational barrier around the C_5- S bond is relatively low for both compounds (maximum 7 kcal.mole^{-1}, see figure 3). So for models **4a** and **4b** ,the reactive sites C_{rad} and the C_3 carbon in the double bond probably stay within a distance favourable to cyclization for a similar amount of time. The minimal distances between the reactive sites , C_{rad}-C_3 are respectively 2.70 and 2.50 Å for **4a** and **4b** [21]. This variation of the C_{rad}-C_3 length is the consequence of structural constraints imposed by the phenyl group in the 5-exo position, in particular the modification of the valence angles C_4-C_5-S which is 111.1° for the CN substituent and 109.4° for a phenyl substituent. This effect is comparable to the Thorpe-Ingold[22,23] effect observed during the formation of small rings. Apparently the effectiveness of the cyclization reaction depends markedly on the distance between the reactive sites : decreasing distances lead to increasing values for k_{cycl}. This parallels other observations done on cyclization involving intramolecular hydrogen transfer.[24]

CONCLUSION

5-*(exo)*-cyano or phenyl-5-*(endo)*-isopropylsulfonyl-2-norbornenyl derivatives are particularly interesting to lead to highly efficient α-sulfonyl carbon centered radical clocks. X-ray determinations and force field calculations suggest that the more rapid rate of cyclization measured in the case of a 5-*(exo)*-phenyl substituent is mainly due to the effect of this group which pushes the whole *endo*-substituent toward the double bond of the norbornenyl group.

EXPERIMENTAL SECTION

General methods. Dry tetrahydrofuran was obtained immediatly prior to use from refluxing over lithium aluminumhydride during 12 hours, followed by distillation and storage over 4Å molecular sieves. Commercial use (anhydrous grade) benzene and perhaloalkanes were stored over 4Å or 3Å molecular sieves. Triethylamine was distilled before use over potassium hydroxide. Cyclopentadiene was prepared from the commercially available dimer after cracking and distillation (40-45°C, 760 mmHg). Acetophenone and alkyl thiols were distilled before use. Other materials were obtained from commercial sources and were used without further purification. Column chromatography was performed on Merck 60 silica gel (70-230 mesh). ^{1}H NMR for intermediates were recorded at 60 MHz on a Varian EM-360A spectrophotometer. High resolution ^{1}H NMR (compounds **1**, **3**, **4**) and ^{13}C NMR were recorded on a Bruker AM200 spectrophotometer at 200 and 50 MHz , respectively. The solvent for these NMR spectra is $CDCl_3$ and data are given in the following order : chemical shifts (in ppm downfield from internal tetramethyl silane using the δ scale), number of protons, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, hept: heptuplet, m: multiplet), coupling constants in Hertz.

X-Ray crystallography. a) Single crystals of **4a** were prepared by slow evaporation from ethanol.They were triclinic, space group P-1, with a = 6.336(3) Å, b = 8.448(4) Å, c = 11.449(3)Å, α = 109.5(1)°, β = 98.1(2)°, γ = 98.5(3)° and d_{calcd} = 1.338 gcm^{-3} for Z = 2 (Mr : 225.31). The intensity data were measured on a CAD4 Enraf-Nonius diffractometer (M_o radiation, monochromated, θ–2θ scans). The size of the crystal used for data collection was approximately 0.4x0.2x0.4 mm^3. A total of 1962 independent reflexions were measured for θ ≤ 25°, of which 1447 were considered to be observed [I ≥ 3σ(I)]. The structure was solved by direct methods by using Multan 80 [25], and refined by full matrix least-squares methods. The last refinements (with an anisotropic thermal agitation factor for non hydrogen atoms) were carried after placing H atoms in their theoretical positions. Hydrogen atom contributions were included in the structure factor calculations but their parameters were not refined.Then agreement factors are : $R = (|F_o - |f_c|) / |F_o = 0.044$ and $R_\omega = [\ \omega(|F_o|-|F_c|)^2 / \omega(|F_o|^2]^{1/2} = 0.064$. The function to minimize being $\omega(|F_o| - |F_c|)^2$.

b) Single crystals of **4b** were prepared by slow evaporation from ethanol . They were orthorombic, space group Pbca, with a = 12.363(4) Å, b = 26.127(3) Å, c = 9.037(5) Å, and d_{calcd} = 1.258 gcm^{-3} for Z = 8 (Mr : 276.4). The procedure used was the same as in the preceding paragraph with a crystal of approximately 0.2X0.2X0.6 mm^3. 2850 independent reflexions were measured for $\theta \leq 26°$,1298 were considered to be observed ($I \geq 3\sigma(I)$). The final discrepancy indices were R' = 0.083 and R_{ω} = 0.085.

1-isopropylthio-1-phenyl ethylene (**5**) A mixture of isopropylthiol (8.92g, 0.117 mol) and triethylamine (25.3g, 0.25 mol) in dry THF (400 mL), is added dropwise into a vigorously stirred solution of acetophenone (12.7g , 0.105 mol) and tetrachlorotitanium (20.7g, 0.125 mol) in dry THF (800 mL). The apparatus is kept at room temperature under a nitrogen atmosphere. After being stirred for 5 additional hours, this solution is poured into cold water, extracted with diethylether, and the organic layer washed with water and dried over $MgSO_4$.The solvent is then removed under vacuum and the pure sulfide is obtained from a reduced pressure distillation (18.1, yield : 97%) . $bp_{0.05}$ = 50°C .^{1}H NMR : 1.28 (6H, d, J = 7.0), 3.03 (1H, hept, J = 7.0), 5.32 (1H, s apparent), 5.50 (1H, s apparent), 7.20 -7.70 (5H, m).

1-isopropylsulfonyl-1-phenyl-ethylene (**6**).To a solution of the sulfide (10.9g, 0.061mol) in CH_2Cl_2 (80 mL) at -20°C, a solution of m-chloroperbenzoïc acid (28g, 0.134 mol) in CH_2Cl_2 (600 mL) is added dropwise. The reaction is kept at this temperature for 0.5 hour. After cooling to -60°C the reaction mixture is filtered off, washed with 5% NaOH solution , then with water and dried over $MgSO_4$.The solvent is removed on a rotatory evaporator to give the crude sulfone to be used without further purification. **6a** (11.4g, yield : 89%) . ^{1}H NMR : 1.25 (6H, d, J = 7.0), 2.84 (1H, hept, J = 7.0), 6.06 (1H, s apparent), 6.48 (1H, s apparent), 7.10 -7.70 (5H, m). .

5-(endo)isopropylsulfonyl-5-phenyl-2-norbornene(4b).A stirred solution of the sulfone (6.10g, 0.048mol) in cyclopentadiene (40g, 0.52mol) is refluxed for 8 hours. At the end of the reaction, dicyclopentadiene is evaporated under reduced pressure and the crude sulfone purified by flash chromatography on silica gel with CH_2Cl_2 as eluent (11g, yield : 84%). High resolution NMR (integration of ethylenic protons) allows the determination of N/X (exo-sulfone/endo-sulfone) = 81/19 . Pure endo and exo isomers are obtained from liquid chromatography on silica gel (eluent CH_2Cl_2). Endo-sulfone (10% yield/**6**): mp 124-125°C, exo-sulfone(60% yield): mp 106-107°C. Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29; S, 11.60. Found : C, 69.60; H,7.20; S, 11.55.^{1}H NMR : 1.04 (3H, d, J = 6.8), 1.10 (3H, d, J = 6.8), 1.16 (1H, d, J = 9), 1.39 (1H, ddt, J = 9, 2.7, 1.8), 2.22 (1H, dd, J = 12.6, 2.7), 2.38 (1H, hept, J = 6.8), 2.78 (1H, dd, J = 12.6, 4), 3.05 (1H, m), 6.39 (2H, m), 7.30 - 7.50 (3H, m), 7.55 -7.75 (1H,m), 7.90 -8.10 (1H, m).^{13}C NMR : 14.4 (q), 16.5 (q), 35.2 (t), 43.5 (d), 48.3 (t), 50.8 (d), 54.6 (d), 76.7 (s), 128.5 (d), 129.2 (d), 130.0 (d), 132.9 (d), 138.5 (s), 139.1 (s).

5-(endo)-(1'-chloro-1'-methylethyl)sulfonyl-5-phenyl-2-norbornene (**1b**) 1.5ml of hexane solution (1.6mol l^{-1}) of n-butyllithium (0.00235 mol) is added dropwise to a well-stirred solution of endo-sulfone **4**(0.65g, 0.00235 mol) in THF (10ml) at -70°C. A solution of C_2Cl_6 (1.7g, 0.0071 mol) in THF (15 ml) is then added dropwise. After 2 hours stirring, the mixture is allowed to return to room temperature. The solution is diluted with diethylether, acidified with HNO_3 (0.1mol l^{-1}), the aqueous layer is extracted with diethylether. The organic layers are washed with water, dried over $MgSO_4$ and evaporated under reduced pressure.The excess of C_2Cl_6 is removed on a rotatory evaporator at 50°C/1.5mm to give the white cristaline halogenated sulfone, and the sulfone is washed with pentane (0.643g, 88% yield) . mp : 71-72°C. Anal. calcd for $C_{16}H_{19}ClO_2S$: C, 61.82; H, 6.16; Cl, 11.41; S, 10.32. Found : C, 61.90; H, 6.11; Cl, 11.35; S, 10.41. ^{1}H NMR : 1.02 (3H,s), 1.18 (1H,d, J = 8.7), 1.40 (2H, ddt, J = 8.7, 2.9, 1.7), 1.51 (3H, s), 3.39 (1H, dd, J = 13.1, 2.9), 2.91 (1H, dd, J = 13.1, 4.0), 3.03 (1H, s wide), 4.01 (1H, s wide), 6.35 (1H, dd, J = 5.7, 2.8), 6.41 (1H, dd, J = 5.7, 3.0). ^{13}C NMR : 28.2 (q),37.5 (t), 43.5 (d), 48.3 (t), 55.2 (d), 79.2 (s), 84.8 (s), 128.3 (d), 128.6 (d), 130.1 (d), 131.6 (d), 132.8 (d), 137.7 (s), 139.0 (d).

6,6-dimethyl-1-phenyl-7-thia-[3.2.1.1^{3,7}]tricyclooctane 7,7-dioxide (**3b**). In a solution of chlorosulfone **1b** (0.400g, 0.00128 mol) in dry, degassed benzene (10 ml) containing a few crystals of A.I.B.N.,one adds 0.51ml of a solution (1.6mol l^{-1}) of tri-n-butyltinhydride (0.00192 mol). The solution is refluxed for 24 hours under a nitrogen atmosphere . After removing the solvent, the residue is dissolved in acetonitrile (10 ml). The solution is washed with dry hexane (3 x10 ml) and evaporated to yield the reduced tricyclic compound **3b** free of tin residue. The crude product is purified by liquid chromatography on silica gel (eluent : petroleum ether / ethyl acetate, 90/10), (0.25g, 72% yield). mp: 123-124°C. Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29; S, 11.60. Found : C, 69.48; H, 7.33; S,11.53. ^{1}H NMR : 1.43 (3H,s), 1.44 (3H,s), 1.57 (1H, dd, J = 13.2, 4.3), 1.71 (2H, m), 1.77 (1H, dt, J = 13.3, 3.9), 2.09 (1H, dt, J = 13.3, 3.5), 2.43 (1H, m), 2.45 (1H, m), 2.82 (1H, d, J = 13.3), 3.37 (1H, m), 7.25 - 7.44 (5H, m). ^{13}C NMR : 21.4 (q), 26.7 (q), 30.1 (t), 37.1 (d), 39.5 (t), 44.4 (d), 44.9 (t), 47.8 (d), 60.9 (s), 74.6 (s), 126.9 (d), 127.8 (d), 128.8 (d), 138.8 (s). Complete NMR assignments using correlation techniques have been realised[26].

Evaluation of the cyclization rate of radical 2b.

The procedure is the one described to prepare **3b**, using increasing quantities of n-Bu_3SnH. The chlorosulfone **1b** (0.397g, 0.00128 mol.) and few crystals of azobisisobutyronitrile (AIBN) are dissolved in 10ml of dried and degassed benzene. When the solution is refluxing, the required quantity of tributyltin hydride is added. The mixture is refluxed for 24 hrs. The solvent is removed under vacuum, the crude product dissolved in 10ml of acetonitlile and washed three times with hexane in order to eliminate tin residues.The solvant is then evaporated under vacuum.The ratio **4b** / **3b** is determined on the crude product from high resolution ^{1}H NMR analysis. For[Bu_3SnH] / [**1b**] = 20, 50 and 100 respectively the relative yield of **4b** is <1%, 3% and 7%.

MM2 calculations.

Geometrical parameters : For **4a** and **4b** we have used X-ray structure parameters (see tables 1 and 2) . All the C-H lengths have been fixed to 1.10 Å.

Calculation parameters not included in the MM2 program: (sulfonyl group) stretching force constant for S-O = 9.6 10^5 dyne.cm^{-1} .[27] Bending : (non indiced carbon are sp^3 type) : CCS=0.55; CspCS= 0.50; CSO= 0.50; CSC= 0.7; OSO=0.7 ; OSC= 0.7; HCS = 0.50. Standard angles of bending : CCS=109.5; Csp^2CS=106.5; CSO =109; CSC = 108.5; OSO=118; SCH= 109.5.

Calculation procedures: For **4a** the minimum in energy has been obtained keeping constant the geometry of the norbornenyl unit (cyano group included) and minimizing the geometry of the isopropylsulfonyl group. Starting from this conformation , rotations Θ around the C_5- S bond are introduced (new values for the coordinates of the oxygen atoms are fixed) and the corresponding energies are calculated by minimizing the conformation of the isopropyl group. For **4b** the same procedure is used but here for each point the phenyl and isopropylsulfonyl groups have been minimized.

atom1	atom2	atom3	angle	atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
C5	S	O1	110.1	S	C5	C6	108.7	C5	C6	C7	96.2
C5	S	O2	106.1	C1'	C5	C4	116.1	C1	C6	C7	99.2
C5	S	C8	108.1	C1'	C5	C6	110.2	C3	C7	C6	95.4
O1	S	O2	117.1	C4	C5	C6	103.2	C1	C2	C3	107.2
O1	S	C8	105.1	C2'	C3	C4'	122.3	C8	C10	H	35.5
O2	S	C8	110.1	C1'	C6'	C5'	120.2	S	C8	C9	112.2
C1'	C2'	C3'	119.3	C4'	C5'	C6'	120.1	S	C8	C10	118.3
C3'	C4'	C5'	119.2	C6	C1	C2	109.1	S	C8	H	95.2
C2'	C1'	C5	122.3	C5	C4	C3	102.2	C9	C8	C10	118.3
C2'	C1'	C6'	119.3	C4	C3	C7	101.4	C9	C8	H	144.2
C5	C1'	C6'	118.2	C4	C3	C2	105.5	C10	C8	H	73.2
S	C5	C1'	108.2	C7	C3	C2	101.3	C10	H	C8	71.2
S	C5	C4	111.1	C5	C6	C1	108.2				

atom1	atom2	distance	atom1	atom2	distance	atom1	atom2	distance
S	C5	1.84	C1'	C5	1.52	C3	C7	1.51
S	O1	1.43	C1'	C6'	1.41	C3	C2	1.53
S	O2	1.43	C5	C4	1.57	C6	C7	1.56
S	C8	1.86	C5	C6	1.59	C9	C8	1.49
C2'	C1	1.40	C6'	C5'	1.42	C10	C8	1.56
C2'	C3'	1.41	C1	C6	1.54	C10	H	1.58
C4'	C3'	1.37	C1	C2	1.31	C8	H	0.96
C4'	C5'	1.39	C4	C3	1.57			

Table 1 : Bond angles (degrees) and bond distances (Å) from X-ray analysis of **4b**.

atom1	atom2	atom3	angle	atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
C2	C1	C6	107.1	C6	C5	C1'	110.0	C5	S	O2	105.8
C1	C2	C3	108.2	C6	C5	S	117.5	C5	S	C8	108.5
C2	C3	C4	106.5	C1	C5	S	106.5	O1	S	O2	118.0
C2	C3	C7	100.3	C1	C6	C5	107.7	O1	S	C8	106.8
C4	C3	C7	101.2	C1	C6	C7	100.3	O2	S	C8	110.0
C3	C4	C5	102.1	C5	C6	C7	98.5	S	C8	C9	114.6
C4	C5	C6	102.7	C3	C7	C6	93.7	S	C8	C10	106.1
C4	C5	C1'	110.7	C5	C1'	N	178.0	C9	C8	C10	111.8
C4	C5	S	109.4	C5	S	O1	107.5				

atom1	atom2	distance	atom1	atom2	distance	atom1	atom2	distance
C1	C2	1.33	C5	C6	1.58	S	O2	1.43
C1	C6	1.52	C5	C8	1.47	S	C8	1.80
C2	C3	1.51	C5	S	1.83	C8	C9	1.51
C3	C4	1.55	C6	C7	1.54	C8	C10	1.52
C3	C7	1.54	C1'	N	1.14	C4	C5	1.57
S	O1	1.44						

Table 2 : Bond angles (degrees) and bond distances (Å) from X-ray analysis of **4a**.

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