slowly at -40 °C to 1.5 mL of a 0.53 M solution of **1a** in the same solvent contained in a 10-mm NMR tube, and the tube was then transferred to the probe of a Bruker 200 MHz NMR spectrometer that was thermostated to -25 °C. A total of 1825 scans were taken at -25 °C. The resulting ^{77}Se NMR had a peak at 565 ppm (relative to Me_2Se) due to unoxidized **1a** and a much stronger peak 289 ppm downfield from this (i.e., at 854 ppm) due to the monooxidation product (**1a**-O). There was also a very weak peak at 847 ppm, which may be due to a product resulting from further oxidation of **1a**-O.

Reaction of 2-Methyl-2-propanethiol with 1a-O. NMR Studies. A 0.5-mL aliquot of a 0.117 M solution of **1a** in $CDCl_3$ was oxidized at -40 °C with sufficient 0.117 M peracetic acid in $CDCl_3$ to lead to the complete disappearance of the singlet for **1a** at δ 1.41. With the solution still at -40 °C, 0.5 mL of a 0.234 M solution of 2-methyl-2-propanethiol in $CDCl_3$ was then added, and the ^1H NMR of the solution was observed as a function of time. The pair of singlets of the oxidation product at δ 1.45 and 1.46 were seen to decrease in intensity, and accompanying this was the appearance and increase in intensity of a singlet at δ 1.41. After 6 h at -40 °C only 1 mol of *t*-BuSH had reacted, the ^1H NMR showed a strong singlet at δ 1.41, and the original pair of singlets at δ 1.45 and 1.46 were gone.

Product Isolation Studies. To a solution of 0.5 g (1.95 mmol) of **1a** in 16.6 mL of reagent grade chloroform was added dropwise at -40 °C 23.6 mL of a 0.1 M solution of peracetic acid in chloroform. After the addition was complete the solution was allowed to stand at -40 °C for several hours, and then 0.35 g (3.88 mmol) of 2-methyl-2-propanethiol in 16.6 mL of chloroform was added dropwise at -40 °C over a 20-min period. After the addition of the thiol the solution was allowed to stand for 4 h. At the end of that time the volume of the solution was reduced to less than 10 mL by rotary evaporation, and the residual solution was subjected to flash chromatography on silica gel using hexane, followed by 3:1 hexane–ether, as eluents. The fraction eluted with hexane (0.34 g) was identical in all respects with a known sample of **1a**. The fraction eluted with 3:1 hexane–ether (0.15 g) was identical in its spectral and other properties with a known sample of *tert*-butyl 2-methyl-2-propanethiosulfinate,[4,7] *t*-BuS(O)SBu-*t*.

Ozonization of 1a. Ozone was generated by passing oxygen through a Monitor Labs NO_x Analyzer ozone unit at a rate of 50 cm^3/min. Calibration was accomplished by passing the resulting O_2/O_3 exit stream through a saturated KI solution and titrating the iodine produced. For ozonization of **1a** 0.10 g of *t*-BuSSeSBu-*t* was dissolved in 5 mL of methylene chloride, and the solution was placed in a midget impinger. The solution was cooled to -78 °C and the O_2/O_3 stream from the ozone generator was passed through the solution for a selected period of time. The exhaust stream from the midget impinger was passed through a bubbler containing saturated potassium iodide. The amount of iodine formed in the bubbler was determined by titration at the conclusion of the experiment. The amount of ozone consumed by the reaction solution, determined by difference from the known rate of O_3 generation (calibration experiment) and the amount getting through to the KI bubbler, was only 40–50% of the amount passing through the reaction solution. This contrasted with the 100% uptake until 1 mol/mol substrate had been taken up that was observed when diethyl sulfide, rather than **1a**, was the substrate.

The ^1H NMR of the final reaction solution was determined at -55 °C in a run in which 1.2 mol of O_3 had been consumed per mol of **1a**. The spectrum showed peaks at δ 1.34, 1.37, 1.41, 1.44, 1.50, and 1.61. The peak at δ 1.41 is due to unreacted **1a** (vide infra). At least one of the other compounds is quite unstable thermally, since warming of the solution resulted in the deposition of a red precipitate (probably selenium).

In a separate experiment 0.26 g of **1a** in 12.5 mL of methylene chloride was treated with ozone at -78 °C until 1.0 mol of O_3/mol **1a** had been taken up by the reaction solution. The final reaction solution was then flash chromatographed on silica gel using 1.5:1 ether–hexane as eluent. The first material eluted (0.114 g) was identical with a known sample of **1a**, and amounts to 44% of the original **1a** being recovered unreacted. The only other material that could be eluted from the column (0.015 g) was shown to be identical with a known sample of *tert*-butyl 2-methyl-2-propanethiosulfinate,[4,7] *t*-BuS(O)SBu-*t*. The inability to elute additional compounds suggests that they decomposed on the column.

Acknowledgment. The ^{77}Se NMR experiments were conducted at the Department of Chemistry of Colorado State University. We deeply appreciate the assistance provided by Dr. Chris Rittner, the Director of the NMR Instrument Facility in the Department of Chemistry at Colorado State University, in carrying out these experiments.

Supplementary Material Available: ^{13}C NMR spectrum of the monooxidation product of *t*-BuSSeSBu-*t* (1 page). Ordering information is given on any current masthead page.

Occurrence of Single-Electron Transfer during the Reduction of α-Halo Sulfones with Zinc

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In order to study the frontier between inner sphere (polar) and outer sphere (monoelectronic transfer) mechanisms, the reduction of α-halo sulfones with zinc has been investigated using as starting materials 5-*endo*-[(1′-halo-1′-methylethyl)sulfonyl]-5-*exo*-cyano-2-norbornenes **1**, efficient radical clock precursors. For the bromo as well as for the chloro sulfone, the tricyclic compound characteristic of the rearrangement of a radical intermediate has been detected: the yields are lower in methanol (1–2%) than in hexamethylphosphoramide (3–11%). These reductions could therefore proceed at least partly, via two monoelectronic transfers leading to the intermediate α-sulfonyl carbanion.

When alkyl halides react with nucleophiles, attack on the carbon center with displacement of the halide ion is usually observed. But, if the normal S_N2 reaction on the carbon is made difficult or if appropriate nucleophiles are selected, nucleophilic substitution at X may take over. This kind of reactions, named substitutions on "positive" halogen[1] or X-philic reactions,[2] may occur chiefly in the presence of substituents which stabilize the carbanion and if the carbon atom is made less accessible by bulky groups. α-Halo sulfones are well known to undergo nucleophilic

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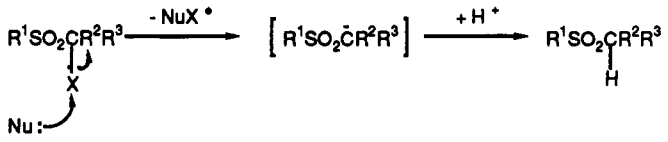
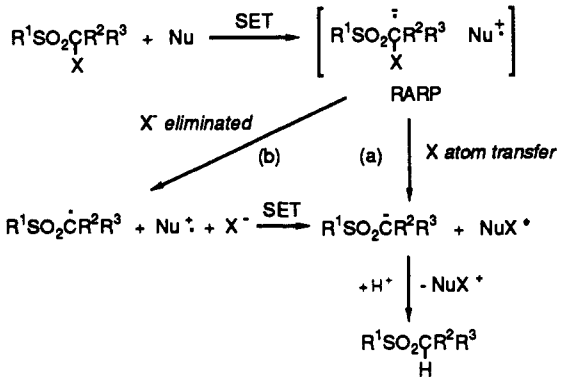
Scheme I

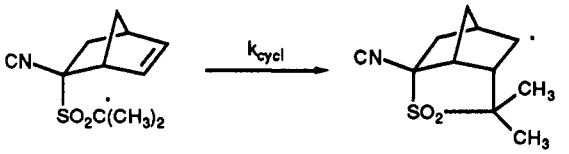


Scheme II



attack on the halogen atom since the effect of the sulfonyl group is such that it not only stabilizes the incipient carbanion but it also hinders normal S_N2 reactions at the α-carbon atoms.[3] Numerous reports in the literature describe the reduction of α-halo sulfones by removal of a "positive" halogen atom in the presence of a proton donor (protic solvents or water–DMF mixtures): alkoxide ions[3-5] in alcohol, mercaptide or thiophenoxide ions,[3,5-7] piperidine,[3] phosphines,[6,8-12] sodium arene sulfinates,[13] sulfite anion[6,8,14] have been used as nucleophiles. All these reactions are supposed to follow the mechanism reported on the Scheme I. This proposal is based upon the stereoselectivity observed by Bordwell et al.[6,8] during the reduction of α-bromo-α-methylbenzyl sulfones with zinc, thiolate anions, phosphines, or sulfite ions in protic solvents. The retention obtained is consistent with a wealth of data showing that α-sulfonyl carbanions are protonated with retention of configuration in protic solvents,[15] Meyers et al.[16,17] have also studied the reduction of α-halo sulfones with zinc or sulfite anion in protic solvents and confirmed that these reactions proceed through the formation of α-sulfonyl carbanions (α-D sulfones are obtained when deuterated methanol is used). These authors confirmed the retention of configuration observed[6,8] in the case

Scheme III



of α-bromo-α-methylbenzyl sulfones (R^1 = Ph, R^2 = Me, R^3 = Ph) but observed a racemization during the reduction of α-bromoalkyl sulfones (R^1 = Ph, R^2 = Me, R^3 = *n*-hexyl). On the other hand, other authors[14] proposed an inversion of configuration for the reduction of the last sulfone (R^1 = *p*-$CH_3C_6H_4$, R^2 = Me, R^3 = *n*-hexyl) by sulfite anions in methanol, and the origin of this discrepancy is not clear.[15]

The racemization observed during the reduction of α-bromo-α-alkyl sulfones, hints at a radical intermediate because C-centered α-sulfonyl radical have been shown to be configurationally unstable.[18] To rationalize these apparently conflicting stereochemical observations, Meyers[17] proposed a mechanism involving a radical anion–radical pair (RARP, Scheme II). After a first electron transfer, the RARP would lead to the intermediate carbanion through two possible pathways. Path a involves an X atom transfer from a radical anion to give directly the carbanion; it would be favored by enhanced carbanion stability (R^2 or R^3 = C_6H_5) and C–X bond strength (C–Cl vs C–Br). Path b involving an X^- elimination followed by a fast electron transfer would be favored by reduced carbanion stability (R = alkyl) and C–X bond strength (C–Br vs C–Cl). Paths a and b would lead respectively to retention and racemization at the carbon α to SO_2.

In order to check the occurence of this mechanism we performed the reduction of α-halo sulfone 1 which allows to trap the eventually formed radical by intramolecular cyclization. The presence of free-radical intermediates in a reaction may be shown by the use of a variety of unsaturated radical clocks[19] generated from alkenyl halides. Several interfering reactions can however compromise the use of these radical probes;[20] it is therefore necessary to make sure that the trapped radicals are actual intermediates between reagents and products. We have designed[21,22] highly efficient radical traps built on the norbornenyl framework (Scheme III); they undergo a very rapid intramolecular cyclization. Thus, the cyclization rate (k_{cycl}) of the α-sulfonyl C-centered radical produced from 5-*exo*-cyano-5-*endo*-[(2-methylethyl)sulfonyl]-2-norbornene reaches 2×10^8 s^{-1} (80 °C);[22] this is one of the fastest radical clocks involving the addition of an alkyl radical on a double bond.[19d] This efficiency is mainly due to two structural factors: (1) three out of the five bonds involved in the cyclization are conformationally frozen, (2) bond lengths C–SO_2 are about 1.82 Å and these lengths compared with free radical clocks where SO_2 is replaced by a carbon (corresponding value 1.54 Å) place the forward radical in closer proximity of the norbornenyl double bond.

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Scheme IV

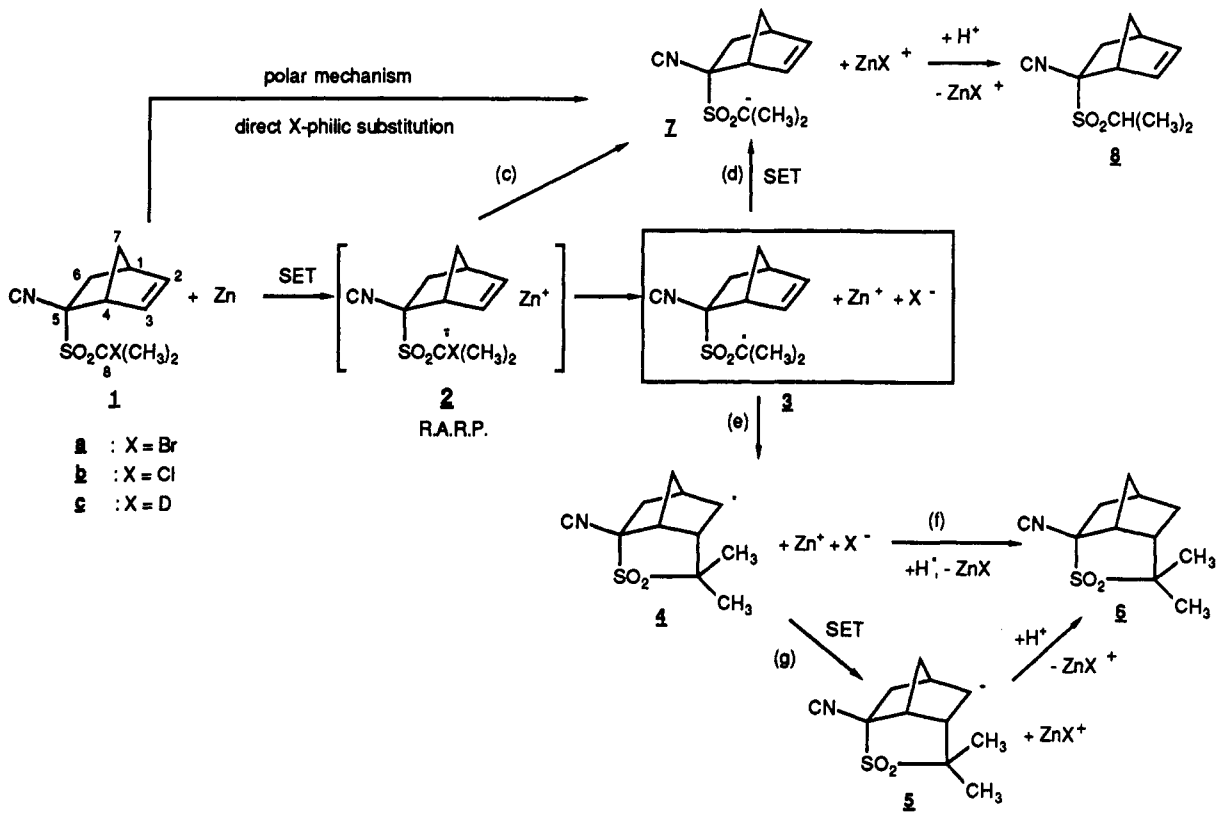

Table I. Data from MNDO Calculations Related to 1b[a]

molecular orbital	E_{MO} (eV)		coefficients of atomic orbitals					
			C5	S	O1	O2	C8	C1
first unoccupied (LUMO)	-2.52	s	-0.18	0.42	0.00	0.00	-0.19	0.00
		p_x	0.14	-0.20	0.15	0.18	-0.44	0.09
		p_y	0.23	0.14	-0.23	0.01	0.02	-0.01
		p_z	-0.38	-0.21	0.11	0.23	0.09	0.01
second unoccupied	-0.67	s	-0.09	-0.02	0.00	0.01	0.28	-0.07
		p_x	0.08	0.32	-0.14	-0.16	-0.01	-0.27
		p_y	0.11	0.09	-0.02	-0.06	0.10	0.10
		p_z	-0.18	-0.26	0.11	0.07	-0.53	-0.45

[a] See Scheme IV. Only coefficients of prevailing atomic orbitals (AO) of the two lowest unoccupied molecular orbital (MO) are reported. E_{MO} is the energy of the considered MO (eV).

Taking into account the results obtained by Meyers et al., the sulfone 1 bearing an isopropyl group would react through the process b (Scheme II), especially when X = Br. The intermediate 3 would follow two possible pathways (Scheme IV). Path d leads directly to the reduced sulfone 8 and path c leads to the tricyclic reduced sulfone 6 via cyclization of the C-centered radical. The choice between these two processes depends upon the relative rates of involved reactions, i.e. electron transfer from Zn^+ to the radical 3, and intramolecular addition of the C-centered radical on the double bond. To check the mechanistic proposition from the literature,[6,16,17] we studied the reduction reactions with zinc in methanol. A single electron transfer process has been proposed as possible pathway during the reduction of *gem*-dihalocyclopropanes with zinc.[23] Reductions in hexamethylphosphoramide (HMPA), a good chelating agent for cationic metals, were also studied, because it has been reported that α-halo sulfones are reduced with fluorenide ions through a radical mechanism in aprotic polar solvents.[24]

MNDO calculations performed on the chlorosulfonyl derivative **1a** show that these compounds are good electron acceptors: energies of the two lowest unoccupied molecular orbitals (MO) are respectively -2.5 and -0.67 eV. If the LUMO corresponds essentially to an orbital displaying an antibonding character between the S atom of the sulfonyl group and the C atom of the isopropyl group, the following MO displays an antibonding character between the Cl atom and the C of the isopropyl group, in agreement with the breaking of this bond when an electron is added on the molecule (Table I).

Results and Discussion

The results obtained for the reduction of the α-bromo or α-chloro sulfonyl radical trap 1 are reported in Table II. As expected, the chloro derivative is more difficult to reduce than the bromo one. For the chloro derivatives, reactions are incomplete in methanol and demand higher temperature in HMPA.

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Table II. Reduction of the α-Halo Sulfones 1 with Zinc

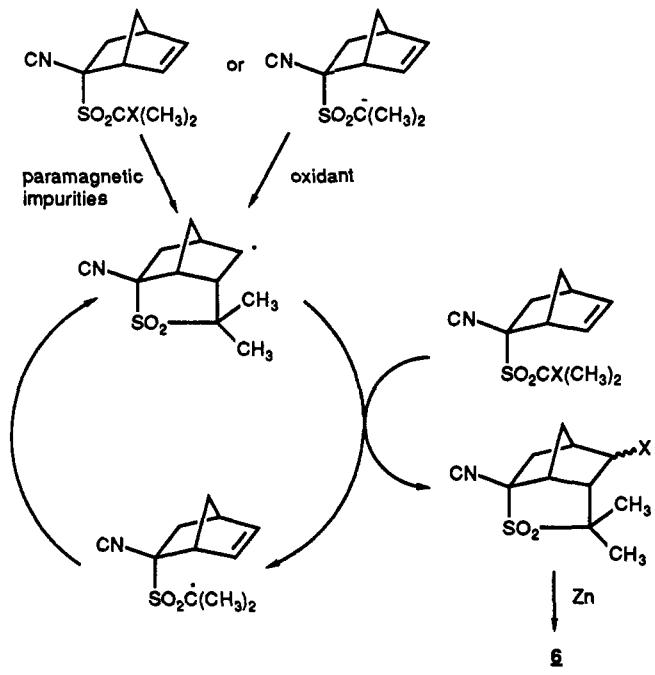
compound	reducer	solvent	t (°C)	time (h)	products (%)[a] 6 (or 9)	8	1
1a	Zn	MeOH	65	18	2	98	-
	Zn	MeOD	65	18	2 (9)	98[b]	-
	Zn	HMPA	20	16	11	89	-
1b	Zn	MeOH	65	22	1.5	61	37.5
	Zn	HMPA	90	20	3	37	60

[a] Relative yields calculated vs the starting halo compound. For 1 and 8 the yield is evaluated from ^1H NMR data, for 6 from GC analysis. [b] Deuterated in the α-position of the sulfonyl group. For the structure of 9, see Scheme V.

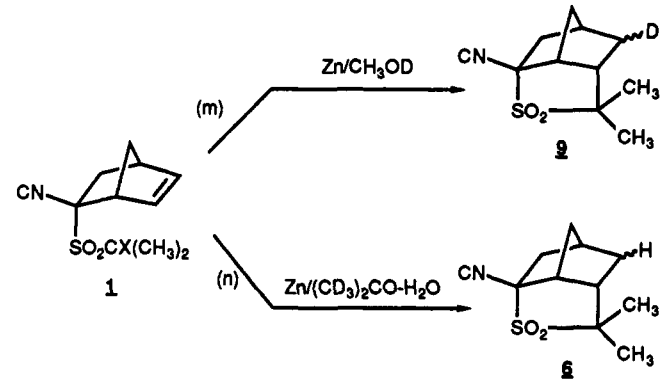
For the studied reduction reactions small amounts of the tricyclic compound 6 are formed in CH_3OH (1–2%). Better yields are obtained in HMPA (3–11%). These yields have been determined by GC using internal standard and by comparison with an authentic sample. A GC–MS analysis has unambiguously proved that the peak used for the measurements corresponds effectively to the tricyclic compound 6. On the other hand, we have verified that 6 is not formed in the medium from the starting halo sulfone in the absence of reducing agent or from the reduced sulfone 8. We verified also that the intermediate carbanion 7 does not undergo an ionic addition to the double bond. Thus, 7 obtained from the addition of sodium methanolate or butyllithium to a solution of 8 respectively in methanol or HMPA does not give 6. To discard the possibility of a deceptive formation of radicals by a pathway different from b (Scheme II) one must check experiments in several directions. First, one must be sure that no oxidant able to oxidize rapidly 7 into 3 (Scheme IV), is present in the solution. In the present study we have checked that when 7 was generated in a methanol or HMPA solution containing the usual amounts of O_2 (i.e. no attempt at degassing the solution), no cyclized products were formed. With a solution saturated in O_2, part of the starting material was decomposed but no evidence for tricyclic compound could be found. This pattern of reactivity would preclude the use of our radical clock for the study of the radical chain oxidation of carbanions in basic medium studied by Russell.[25] To avoid any such kind of problems, all the reported experiments were performed on carefully degassed solutions. Secondly, one must be sure that the radical species 3 are not formed through adventitious paramagnetic impurities reacting on the starting sulfone 1(a or b) via an SH_2 mechanism. These impurities may originate from the reducing reagents and, for this reason zinc of high purity was used (99.999%). We checked that the carbanion 7 generated in the presence of the Zn powder used for the reduction does not yield tricyclic derivatives. The same absence of tricyclic product was observed when Zn was replaced by $ZnCl_2$ (formed during the reaction). Another deceptive origin for the formation of tricyclic compound 6 could be a chain reaction[20] resulting of the reaction of 4 with the starting material via a bimolecular homolytic substitution (SH_2) (Scheme V). This possibility lays the stress on the importance of carefully checked experimental conditions when the polar versus single electron transfer mechanisms are studied which involved carbanions.

During reductions with zinc in CH_3OD, both the uncyclized reduced compound 8 deuterated in α-position of the sulfonyl group and the deuterated tricyclic compound 9 are obtained (Scheme VI). If $(CD_3)_2CO$ is used in place of CH_3OD no trace of 9 is observed; only the nondeuterated tricyclic compound 6 is obtained. After the addition of

Scheme V



Scheme VI



the C-centered radical on the double bond, two possible pathways are available for the cyclized radical 4: abstraction of H• (path f, Scheme IV) or electron supply from the nucleophile Zn^+ (path g) to give the carbanion 5 then rapidly protonated. The described pattern of deuteration shows that only path g occurs. Thus, the first electron transfer is rapidly followed by a second electron transfer leading to a carbanion. This second electron transfer is very fast when Zn^+ is the reducer. The rates of the oxidation of Zn^+ by CH_2OH have been measured to be 10^9 s^{-1}.[26]

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To summarize, in this work we have shown that during the reduction of α-halo sulfones with zinc, radical intermediates are involved. In all the experiments performed, the presence of a rearranged compound, typical of this radical intermediate, has been demonstrated even if the yields are very low when methanol is used as the solvent. We have also to point out that the studied reaction is a heterogeneous reaction in which radicals are formed at the Zn surface and may be further reduced by electrons from the surface. A close analogue is Grignard reagent formation which is certainly a two-step process; here, too, yields of rearranged or cyclized radical products are low.[27] The reduction of halo sulfone by zinc could proceed, at least in part, and in agreement with the proposition of Meyers et al.,[16,17] through two successive monoelectronic transfers leading in the last step to a carbanion which, after protonation, gives the expected reduced sulfone. The use of aprotic polar solvent as HMPA seems to enhance the ability of the reaction to follow a radical mechanism. This solvent effect could be explained in different fashions. The first to be considered is connected with the longer lifetime of carbanions created in aprotic polar solvents in comparison to those created in protic solvents.[28] Under such conditions, if an oxidizing impurity was present it would have more time to transform the carbanion 7 (formed by a polar mechanism) into the radical 3. This possibility must be discarded because of the care that we took in eliminating oxidizing impurities in the medium. Furthermore, when one purposedly adds 20 mol % of chloranil vs the reducer during the reduction reaction of **1a**, nothing is changed for yields of the formed products. This means that the radical process is not a chain reaction. The second possibility could be that HMPA allows a faster escape of the RARP for the radical anion 2. After such an escape the formed radical 3 would have no reducing species in its close proximity (Zn^+) and would therefore stay longer under the radical form which leads to 4. The relative viscosities of HMPA and MeOH are not in the right direction to fit with such an explanation. We have performed the reduction of **1a** in MeOH or HMPA in the presence of appropriate salts ($NaPF_6$) to eventually show the importance of ion pairing[29] in the dichotomy cyclized/uncyclized reduced compound. No significant difference was observed in the ratio 6/8 when adding up to 5 times excess of this salt with respect to the sulfone.

Finally, one may suppose that the crossroad polar mechanism/electron transfer mechanism is earlier than a putative RARP. For this explanation, the competition would be between a totally inner sphere pathway (polar mechanism in Scheme IV) and outer sphere mechanism electron transfer mechanism. The coexistence of such pathways has been proposed several times in the literature.[30] The mechanistic study of polar versus SET mechanisms in the reduction of carbon halogen bonds has now a long story.[31] Beckwith has proposed that in the reduction of halogenoarenes by lithium aluminum hydride polar and SET pathways coexist.[32] In our case this hypothesis is backed by the pattern of reactivity observed upon addition of chloranil to the reacting medium. Indeed, a small amount of added chloranil does not modify anything in the reduction reaction (see above). In contrast, an equimolecular quantity (vs the reducer) of chloranil inhibits the formation of the tricyclic compound **6**, without inhibiting the formation of the uncyclized reduced compound 8 (reduction of **1a** with Zn in MeOH or HMPA). These results hint that at least a part of the reduction reaction is S_N2 like (displacement on "positive" halogen). The radical pathway could, within such an approach result from a different site of interaction between the α-halo sulfone and the Zn surface; SO_2 could play the role of electrophore (hidden ambident reactivity),[33] as suggested by the localization of the LUMO in the SO_2 fragment rather than on the C–Cl bond (Table I).

Experimental Section

General Methods. Dry hexamethylphosphoramide was obtained from distillation on barium oxide under reduced pressure and nitrogen atmosphere and storage over 4-Å molecular sieves. Commercial (anhydrous grade from SDS) benzene and tetrachloromethane were stored over 4-Å or 3-Å molecular sieves. Cyclopentadiene was prepared from the commercially available dimer after cracking and distillation (40–45 °C, 760 mmHg). 99.999% pure powdered (−100, +325 mesh) zinc (from CERAC) was used for the reductions. Other materials were obtained from commercial sources and were used without further purification. Liquid chromatography was performed on an INTERSMAT IGC 121 FL apparatus connected to a DELSI ICR 1B integrator; column: SE 30 10%, 2 m, 150–280 °C, 7 °C min^{-1}, P = 0.7 bar. The analysis in CPG–MS was performed on a RIBERMAG R 10.10C; vector gaz, helium; V = 70 eV; working temperatures: injector, 300 °C; interface, 300 °C, source, 150 °C; column, CPSIL5 CB; temperature range, 150–300 °C, 5 °C min^{-1}. The mass spectrometer was a KRATOS MS 50 type. ^1H and ^{13}C NMR were recorded on a BRUKER AM100 apparatus at 100 and 25 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 tetramethylsilane using the δ scale), number of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; hept, heptuplet, m, multiplet).

5-*endo*-(Isopropylthio)-5-*exo*-cyano-2-norbornene (10) has been prepared by the method described by Stella et al.[34]

5-*endo*-(Isopropylsulfonyl)-5-*exo*-cyano-2-norbornene (8). A solution of **10** (17.8 g, 0.092 mol) in 200 mL of dichloromethane is cooled to 0–5 °C with an ice bath. A solution of *m*-chloroperbenzoic acid (42.2 g (80% purity), 0.184 mol) in cold dichloromethane (0–5 °C) is prepared and stirred for 30 min. The *m*-chlorobenzoic acid residue is filtered off and the solution is added dropwise to the sulfide, keeping the temperature near 5 °C. At the end of the addition, the mixture is stirred during 2 h, the temperature reaching progressively 20 °C. The solution is then cooled to −60 °C and filtered off. This operation is realized three times. The residual solution is washed three times with 200 mL of 5% solution of aqueous sodium hydroxide solution and

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then two times with 100 mL of water. After drying on magnesium sulfate, the dichloromethane is evaporated under reduced pressure. The crude product (15.1 g, 73% yield), as an oil, crystallizes on standing. The pure *endo* isomer is obtained after three crystallizations in a pentane–diethyl ether mixture, mp 63–64 °C. Anal. Calcd for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71; N, 6.22; S, 14.23. Found: C, 58.57; H, 6.69; N, 6.10; S, 14.25. ^1H NMR: 1.41 (3 H, d, J = 6.9), 1.45 (3 H, d, J = 6.9), 1.71 (1 H, ddt, J = 9.1, 2.7, 1.5), 1.81 (1 H, d, J = 9.1), 2.08 (1 H, dd, J = 12.6, 2.7), 2.47 (1 H, dd, J = 12.6, 2.7), 3.20 (1 H, s), 3.74 (1 H, s), 3.76 (1 H, hept), 6.13 (1 H, dd, J = 5.6, 2.9), 6.36 (1 H, dd, J = 5.6, 3.1). ^{13}C NMR: 14.6 (q), 16.6 (q), 39.1 (t), 43.5 (d), 49.3 (t), 53.8 (d), 53.9 (d), 63.8 (s), 120.1 (s), 130.7 (d), 139.3 (d).

5-*endo*-[(2-Chloro-2-methylethyl)sulfonyl]-5-*exo*-cyano-2-norbornene (1b). This compound has been prepared by a phase transfer catalyzed reaction from the sulfone 8. Aqueous phase: 20 mL of a 50% sodium hydroxide solution and tetra-*n*-butylammonium bromide (0.142 g, 0.00044 mol). Organic phase: 20 mL of tetrachloromethane and sulfone 8 (1 g, 0.0044 mol). The mixture is vigorously stirred at 20 °C during 6 h. At the end of the reaction the organic layer is decanted and the aqueous phase extracted with 40 mL of dichloromethane. The organic layers are washed twice with 20 mL of water, dried on magnesium sulfate, and concentrated under vacuum. The crude product is dissolved in a small amount of benzene and chromatographed on silica gel (benzene as eluent). The solvent is evaporated under reduced pressure. The pure chloro compound **1b** crystallizes on standing (0.82 g, 71% yield), mp 45–46 °C. Anal. Calcd for $C_{11}H_{14}ClNO_2S$: C, 50.86; H, 5.43; N, 5.39; S, 12.35; Cl, 13.65. Found: C, 50.80; H, 5.47; N, 5.42; S, 12.29; Cl, 13.61. ^1H NMR: 1.72 (1 H, ddt, J = 9.7, 2.8, 1.7), 1.89 (1 H, d, J = 9.7), 2.03 (3 H, s), 2.18 (3 H, s), 2.20 (1 H, dd, J = 13.1, 2.8), 2.62 (1 H, dd, J = 13.1, 3.7), 3.20 (1 H, s wide), 3.85 (1 H, s wide), 6.13 (1 H, dd, J = 5.5, 2.74), 6.38 (1 H, dd, J = 5.5, 3.2). ^{13}C NMR: 28.3 (q), 29.1 (q), 40.6 (t), 43.2 (d), 49.2 (t), 54.9 (d), 63.9 (s), 85.3 (s), 120.1 (s), 130.7 (d), 139.4 (d).

5-*endo*-[(2-Bromo-2-methylethyl)sulfonyl]-5-*exo*-cyano-2-norbornene (1a). The sulfone 8 (1.5 g, 0.00664 mol) and tetrabromomethane (5 g, 0.015 mol) are dissolved in 20 mL of *tert*-butyl alcohol. To this vigorously stirred solution one adds at 25 °C powdered potassium hydroxide (1 g, 0.0178 mol). After 1 h the mixture is diluted with diethyl ether and slowly hydrolyzed. The aqueous layer is extracted with diethyl ether. The combined organic layers are washed with water, dried on magnesium sulfate, and concentrated under reduced pressure. The residual yellow oil is purified by liquid chromatography on silica gel (benzene as eluent). Two fractions of the pure bromo compound are obtained. Endo:exo ratios are respectively 85:15 and 94:6. The overall yield is 55%, mp of the 94:6 (N/X) mixture of **1a** 57–58 °C. Anal. Calcd for $C_{11}H_{14}NO_2SBr$: C, 43.43; H, 4.64; N, 4.60; S, 10.54; Br, 26.27. Found: C, 43.50; H, 4.66; N, 4.52; S, 10.45; Br, 26.23. ^1H NMR: 1.75 (1 H, ddt, J = 9.6, 3.0, 1.6), 1.89 (1 H, d, large, J = 9.6), 2.18 (3 H, s), 2.27 (1 H, dd, J = 13.1, 3.0), 2.35 (3 H, s), 2.66 (1 H, dd, J = 13.1, 3.7), 3.20 (1 H, s large), 3.86 (1 H, s large), 6.16 (1 H, dd, J = 5.6, 2.8), 6.39 (1 H, dd, J = 5.6, 3.7, 3.1, 1.6). ^{13}C NMR: 29.9 (q), 31.0 (q), 41.6 (t), 43.7 (d), 49.3 (t), 55.6 (d), 64.8 (s), 76.6 (s), 130.9 (d), 139.6 (d).

1-Cyano-6,6-dimethyl-3,8-methano-7-thiatricyclo[3.2.1]octane 7,7-Dioxide (6). In a solution of chloro sulfone **1b** (0.333 g, 0.00128 mol) in dry, degassed benzene (10 mL) containing few crystals of AIBN, one adds 1.2 mL of a solution (1.6 mol L^{-1}) in hexane of tri-*n*-butyltin hydride (0.00192 mol). The solution is refluxed for 25 h under a nitrogen atmosphere. After removing the solvent, the residue is dissolved in acetonitrile (10 mL). The solution is washed with dry hexane (3 × 10 mL) and evaporated to yield the reduced tricyclic compound free of tin residue (0.188 g, 65% yield). The crude product is recrystallized in ethanol, mp 138–139 °C. Anal. Calcd for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71; N, 6.22; S, 14.29. Found: C, 58.68; H, 6.69; N, 6.21; S, 14.3. ^1H NMR: attributions are not complete here, correlations ^{13}C–^1H and ^1H–^1H are necessary to obtain a full attribution,[35] 1.42 (3 H, s), 1.44 (1 H, m), 1.50 (3 H, s), 1.69–1.94 (3 H, m), 2.23 (1 H, dt), 2.40 (1 H, dt), 2.47–2.59 (2 H, m), 3.27 (1 H, m). ^{13}C NMR: 20.9 (q), 25.9 (q), 29.1 (t), 36.4 (d), 39.9 (t), 42.5 (t), 48.4 (d), 49.6 (d), 62.7 (s), 63.2 (s), 116.6 (s). The crystallographic data of this compound has been published.[36]

Typical Reduction Reactions with Zinc. (a) Reductions in Methanol as Solvent. In a solution of the halo sulfone **1a** or **1b** (0.001 mole) in 20 mL of **6** in degassed methanol are added powdered Zn (0.005 mol) and then 10 μL of concentrated sulfuric acid. The mixture is stirred and refluxed under N_2 atmosphere during 18 or 22 h (see Table II). The zinc residue is filtered off. The filtrate is concentrated under reduced pressure.

Reduction of 1a: weight of crude product, 0.226 g (yield 96%). The ^1H NMR spectrum is in agreement with the structure of the compound 8. The tricyclic compound is not detectable here by ^1H NMR; 6 is quantitatively analyzed by GC (see later). A recrystallization in pentane–diethyl ether mixture leads to pure 8.

Reduction of 1b: weight of crude product, 0.230 g. A ^1H NMR analysis indicates the presence of the starting **1b** and 8 in the ratio 40:60, approximatively. The tricyclic compound is not detected by this method. A liquid chromatography on silica gel (benzene–ethyl acetate (95:5)) affords successively the unreacted chloro derivative **1b** (0.090 g) and the reduced compounds (8 + 6, 0.130 g, 89% yield vs the effectively used chloro sulfone).

(b) Reductions in HMPA as Solvent. The same quantities of starting materials as described above are used, but 20 mL of HMPA are added in place of methanol. See Table II for time and temperature of reaction. At the end of the reaction we dilute with 40 mL of diethyl ether. The organic layer is washed two times with water, dried with $MgSO_4$, and concentrated.

Reduction of 1a. The crude product contains 8 and 6; weight, 0.205 g (91% yield). The ^1H NMR indicates a ratio 8/6 = 90:10. See later for the quantitative analysis of 6.

Reduction of 1b: weight of crude product, 0.240 g. A ^1H NMR analysis indicates the presence of the starting **1b**, and 8 + 6 in the ratio 60:40, approximatively. A liquid chromatography on silica gel (benzene–ethyl acetate (95:5) as eluent) affords successively the unreacted chloro derivative **1b** (0.120 g) and the reduced compounds (8 + 6, 0.106 g, 88% yield vs the effectively used chloro sulfone).

General Procedure for the Determination of Relative Yields of Reduced Compounds Obtained during the Reduction of 1a and 1b. In order to measure quantitatively the tricyclic compound 6 formed during the reductions of compounds **1a** and **1b** we used as internal standard $C_{20}H_{42}$ having a retention time similar to the one of 6 under our GC conditions. First, a calibration curve between $C_{20}H_{42}$ and 6 was obtained using a solution of $C_{20}H_{42}$ in CH_2Cl_2 (0.0025 mol L^{-1}) containing 1, 2, 4, 6, 8, and 10 mol % of 6. The identification and the dosage of the uncyclized reduced sulfone 8 and of the starting halo compound were performed, when necessary, by ^1H NMR analysis.

Zn as Reducer, Methanol as Solvent. A 0.00025-mol portion of the halo compound **1a** or **1b** dissolved in 5 mL of methanol is placed in a 20-mL Schlenk's tube. Powdered Zn (0.00115 mol) is added and the mixture degassed three times under vacuum (0.01 mmHg) at the temperature of the liquid air followed by warming up to room temperature. Concentrated sulfuric acid (2 μL, about 0.00007 mol) is added. The mixture is stirred and refluxed under N_2 atmosphere during 20 h. Then the zinc residue is filtered off. The filtrate is concentrated under reduced pressure and the crude product dissolved in dichloromethane (20 mL). The solution is dried with magnesium sulfate and evaporated. The crude product is dissolved in exactly 5 mL of the standard solution of $C_{20}H_{42}$ (0.0025 mol L^{-1}) in dichloromethane. The yield of tricyclic compound 6 is measured by GC analysis using the calibration curve. The data given in Table II are the average of three determinations. We have verified that (i) the halo compounds **1a** and **1b** and the linear reduced product 8 which decomposes in the conditions of the GC analysis do not give the tricyclic compound 6; (ii) under the conditions of reaction, 8 do not lead to the formation of the tricyclic compound 6; (iii) the peak taken into account for the determination of the yield of 6 gives the same mass spectra as the pure 6 (CPG–MS analysis). On the other hand, the linear reduction compound 8, the main product of the reaction is

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identified by its ^1H NMR parameters. Note that the ratio exo:endo is unchanged between the halogeno compound and the reduced sulfone 8.

Reductions with Zn in HMPA as Solvent. The quantities of halo compound **1a** or **1b** and reducer were the same as described for the reduction reactions in methanol, but 5 mL of HMPA are used here as solvent. The temperature and time of reaction are indicated in Table II. At the end of the reaction we diluted with 10 mL of diethyl ether. The organic layer is washed two times with 20 mL of water, dried with magnesium sulfate, and concentrated under reduced pressure. The crude product is dissolved in exactly 5 mL of the standard solution of $C_{20}H_{42}$ (0.0025 mol L^{-1}) in dichloromethane. The yield in tricyclic compound **6** is measured by GC analysis using the calibration curve. It has been verified that, under the conditions of the reaction, the linear reduced compound **8** does not yield the tricyclic sulfone **6**.

Reductions in Deuterated Solvents. The chloro derivative **1b** has been reduced with Zn under the same conditions as the ones described above using 0.00005 mol of **1b** and 0.00025 mol of Zn. Solvents used for reaction m, 1 mL of CH_3OD, and for reaction n, 1 mL of $(CD_3)_2CO$. The identification of the deuterated tricyclic compound **9** (reaction m) and of the protonated tricyclic compound **6** (reaction n) has been realized with the help of coupled MS-GC.

Experiments performed in order to verify that the tricyclic reduced sulfone is not formed in the absence of reducer or directly from the intermediate carbanion.

(a) A solution of **1a** (38 mg) in 2.5 mL of CH_3OH is heated at 65 °C during 20 h. The recovered product is analyzed by ^1H NMR and GC. No trace of the compound **6** is detected.

(b) **8** (22.5 mg, 0.0001 mol) is heated during 6 h in 2 mL of CH_3OH containing 5.4 mg (0.0001 mol) of CH_3ONa. After hydrolysis and extraction the starting material is recovered without modification. (c) **8** (56.2 mg, 0.0025 mol) is dissolved in 5 mL of HMPA. The solution is degassed as for the reduction reactions. A solution of BuLi in hexane is added (169 μL of a solution 1.6 mol L^{-1}, 0.00027 mol). A pale yellow color appears. The solution is stirred during 3 h at room temperature. After the usual treatments, no trace of the tricyclic compound **6** is detected on GC analysis. The same result is observed when zinc (37.6 mg, 0.00057 mol) and $ZnCl_2$ (77.7 mg, 0.00057 mol) are added in the medium.

Salt Effects on the Reduction of 1a. **1a** (30.4 mg, 0.0001 mol) is dissolved in 2 mL of MeOH. Zn (30.1 mg, 0.0005 mol) and $NaPF_6$ (84 mg, 0.0005 mol) are added, and the solution is degassed as described above. Concentrated sulfuric acid (1 μL) is added, and the solution is refluxed during 22 h. After filtration, washing with MeOH followed by evaporation under reduced pressure, the crude product is dissolved in exactly 2 mL of the standard solution of $C_{20}H_{42}$ (0.0025 mol L^{-1}) in dichloromethane. The yield of tricyclic compound **6** measured by GC analysis using the calibration curve is 1%.

The same experiment was performed in HMPA as solvent (2 mL) with same quantities of reagents, but with stirring at room temperature during 22 h. After dilution with water, extraction with diethyl ether, drying of the organic layer with magnesium sulfate followed by evaporation of the solvent, the crude product is dissolved in exactly 2 mL of the standard solution of $C_{20}H_{42}$ (0.0025 mol L^{-1}) in dichloromethane. GC analysis indicates a yield of 5% in the tricyclic compound **6**.

Chloranil Effect on the Reduction of 1a. The same experiments as the ones described for salt effects were performed in MeOH and HMPA with chloranil in place of $NaPF_6$; 0.0001 mol and 0.0005 mol of chloranil were used successively. A 0.0001-mol portion of oxidant had no effect on the ratio **8**/**6** (98/2 in MeOH and 89/11 in HMPA). With 0.0005 mol of chloranil we did not detect the presence of the tricyclic compound **6** in the crude product, and a ^1H NMR analysis indicated the presence of the uncyclized compound **8** (a quantitative analysis was not possible).

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Methyl Effects in the Cyclization of γ-Epoxy Bis-Sulfones

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A quantitative study on the effects of methyl and *gem*-dimethyl groups in the intramolecular ring opening of epoxides by bis-sulfonyl carbanions is reported for the formation of cyclopropanes. Reaction rates are increased by methyl groups on the chain connecting the nucleophile with the oxirane and depressed by methyl substitution in the epoxide ring. When *gem*-dimethyl groups are present on the epoxide, ring opening is apparently inhibited. It will be shown that in this case the reaction is reversible and the apparent stabilization of the *gem*-dimethyl-substituted oxirane is actually due to a combination of effects on both the forward and the reverse reactions. On the basis of current theories on intramolecular reactions, it is suggested that release of ground-state strain and van der Waals repulsions in the transition state can account for the observed reactivity.

The ring closure of bifunctional molecules provides a powerful model for studying the factors that control intramolecular reactivity[2] and for testing, on simple systems, effects, such as proximity and orientation, that have been proposed for explaining the high efficiency of enzymatic catalysis.[3]

We have recently studied the effect of ring size in the intramolecular ring opening of ω-epoxy carbanions, and we have found a marked dependence of regioselectivity and rates upon the length of the chain connecting the nucleophile and the oxirane ring.[4] In this study we examine

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