Mechanistic Investigation of the Reaction between α-Sulfonyl Carbanions and Polyhalogenomethanes. Electron Transfer versus Polar Pathways

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Abstract: A number of α-sulfonyl carbanion precursors, whose structures include a double bond appropriately situated to intramolecularly trap the potential radical formed by 1-e oxidation, have been synthesized and reacted with CCl_4, CBr_4, and $BrCCl_3$ in a *t*-BuOH/*t*-BuOK medium. Although CCl_3 radicals are trapped in this reaction by BHT, none of the cyclized products expected for an electron-transfer (ET) reaction between the α-sulfonyl carbanion and these electrophilic polyhalogenomethanes has been found in the halogenation reaction performed in the presence or absence of a strong magnetic field. The formation of Cl_3^- may be rationalized by the higher reducing ability of Cl_3C carbanion than α-sulfonyl carbanion. This high reducing ability of Cl_3C^- is well accounted for by MNDO calculations. The consequences of these findings are discussed in the perspective of the ET vs polar pattern of reactivity reported in the literature, and they show some of the limits of the criteria used to discriminate the ET-polar dichotomy.

One of the most poorly resolved points in the study of reaction mechanisms in solution is presently the frontier between electron-transfer (ET) processes and polar reactions. Several reactions long thought of as being typically polar have recently been proposed[1] to involve an electron-transfer mechanism. On the other hand, it would seem that some reactions in which an electron transfer between the nucleophile and the electrophile is proposed to take place are possibly deceptive[2] when an analysis with different experimental tools is applied. This raises the fundamental question: when does the distinction between polar and ET mechanisms occur in the succession of elementary steps? This question is relevant to a variety of organic transformations, including direct substitution at sp^3 carbon[3] and S_N1,[4] substitution at O,[5] nucleophilic[6] and electrophilic[7] substitutions on aromatic or heteroaromatic substrates, dediazonization of arenediazonium salts,[8] direct reaction between carbanions and carbenium ions,[9] hydride transfer,[10] nucleophilic additions on carbonyl compounds,[11] Diels-Alder type reactions,[12] Stevens' rearrangement,[13] and even proton transfer[14] or OH^- reactivity.[15] The same ET-polar coexistence of mechanistic pathways has also been identified in the chemistry of organometallic substrates centered on representative[16] or transition metal elements.[17] In inorganic chemistry, the equivalent of ET-polar coexistence has been found for some substrates where both inner sphere and outer sphere electron transfer occur con-

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currently.[18] Using the generalized nomenclature of electron-transfer mechanisms, this question leads to an exploration of the frontier between outer sphere and inner sphere electron transfer.[19] This frontier deserves in-depth studies because recent theoretical propositions suggest that S_N2 type transition states could possibly be viewed as inner sphere electron transfer where the carbon plays the role of a bridge.[20] At least three groups of researchers have independently proposed that there is a continuum between inner sphere and outer sphere type situations of mechanistic schemes.[21] If such is the case, it becomes important first to recognize reactions that could occupy a borderline position in the continuum of mechanisms. Second, when one is found, the study of the experimental parameters which modify the inner sphere/outer sphere ratio of participation in the overall reaction should yield information about the eventual existence of a continuum.

In a first attempt to achieve such an aim, we studied the reaction between the conjugate base of 2-nitropropane and *p*-nitrobenzyl bromide where Kornblum et al. have shown that polar and radical pathways were needed to rationalize the observed facts.[22] For this model we reached the conclusion that *p*-nitrobenzyl halide substrates contained built-in structural ambiguities for the experimental verification of the continuum hypothesis. The overall selectivity may indeed be viewed as the consequence of a competition between an inner sphere process on the benzylic carbon (S_N2) and an outer sphere process (or, possibly, an inner sphere without atom transfer process) where the electron transfer takes place mainly on the aromatic part of the substrate (hidden electrophilic ambident reactivity).[23] So we gave up on *p*-nitrobenzyl halide substrates as candidates for studying the competition between inner sphere versus outer sphere processes on the *same given electrophilic center.*

At this point, CCl_4 appeared to be a better substrate to study this problem. This electrophilic substrate corresponds to the simplest possible structural situation (except, perhaps, dihalogens where the frontier ET–polar situation again appears[24]). Because of the Cl steric hindrance, the only place where a nucleophile could attack is at Cl, and all four Cl are equivalent. Nevertheless, the thermal reactivity of CCl_4 toward various nucleophilic substrates has been rationalized according to a great variety of mechanistic schemes. Depending upon the nucleophile, CCl_4 behaves as an electrophilic substrate able to enter into non-chain radical[25] and radical chain mechanisms[26] as well as non-chain ionic[27] and ionic chain mechanisms.[28] Furthermore, in 1977, C. Y. Meyers and co-workers proposed a unified crossroad of polar and ET pathways for rationalizing the experimental results of halogenation of carbanions. In this proposition, a solvent caged radical–anion radical pair intermediate (RARP) is the molecular crossroad where the discrimination of ET and polar pathways takes place.[29a,f] This author insists on the point that this type of radical intermediate has to be distinguished from a *free* radical to rationalize the observation that chiral α-sulfonyl carbanions are halogenated with retention of configuration.[29b] Such a stereochemical result would

$$\underset{\text{An = anion}}{An^- + CCl_4} \xrightarrow{ET} \underset{\text{cage, initimate RARP}}{[An^\bullet, CCl_4^{\bullet -}]} \longrightarrow AnCl + CCl_3^- \quad (1)$$

usually lead to the conclusion that the reaction of CCl_4 with α-sulfonyl carbanions involves a simple polar type displacement on Cl, viewed as a generalized electrophilic center (other possible nomenclature S_NCl^+).[30a] However, to rationalize other experimental observations (leaving group effects, correlation of rates with redox potentials, trapping of $^\bullet CCl_3$ in the medium, etc.[29a]), C. Y. Meyers and co-workers proposed the preceding RARP hypothesis. This proposition is then supported by the valence bond configuration mixing model, which predicts that CCl_4 should be more prone to react by an electron-transfer pathway than are alkyl chlorides.[20a] Therefore, carbon tetrachloride seemed a suitable substrate to use to find a series of nucleophiles where one could experimentally study this elusive border between outer and inner sphere electron transfers. Furthermore, earlier detailed reports by Hauser and his students specifically describe the reactivity of carbanions (Ph_2CHNa) toward positive halogens (CCl_4) as a straightforward polar mechanism.[31] Thus some clarification is needed.

This publication describes the reactivity of α-sulfonyl carbanions with CCl_4 and other perhaloalkanes using different techniques. All of the data that we have gathered may be rationalized if the reaction between α-sulfonyl carbanions and CCl_4 is a "classical" S_NCl^+[29] without compelling experimental facts for the participation of an outer sphere electron transfer. Several experiments described herein illustrate the risks associated with some experimental criteria commonly used to establish the participation of ET in a reaction.

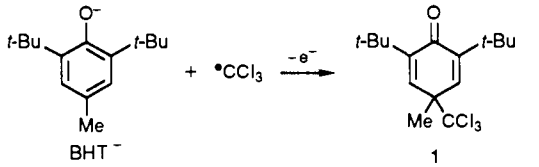
Results and Discussion

1. Trapping of $CCl_3^\bullet$: The Problem. One of the best ways to support the ET hypothesis in the halogenation reaction 1 would be trapping the CCl_3 radicals that escape from the cage:

$$\underset{M^+ = K, Na}{R^1SO_2\bar{C}HR^2, M^+ + ClCCl_3} \longrightarrow \underset{RARP}{[R^1SO_2C^\bullet HR^2, M^+, Cl^-, {}^\bullet CCl_3]} \longrightarrow$$

$$R^1SO_2C^\bullet HR^2, + M^+Cl^- + {}^\bullet CCl_3 \longrightarrow \text{escape from the cage} \quad (2)$$

The support of the ET hypothesis will be effective only if it can be proved that CCl_3 radicals unambiguously originate from this cage. C. Y. Meyers et al. were able to trap CCl_3 radicals (reaction 3) with 4-methyl-2,6-di-*tert*-butylphenoxide anion (BHT^-) during reaction 2.[29c]



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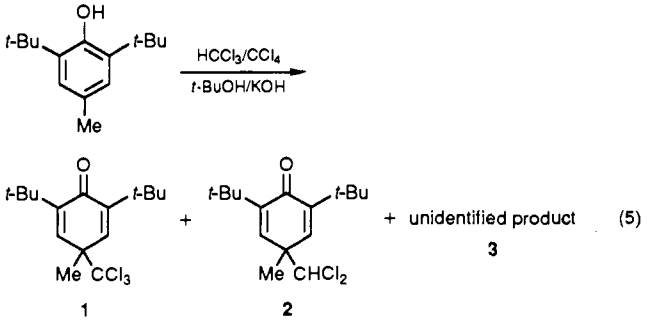
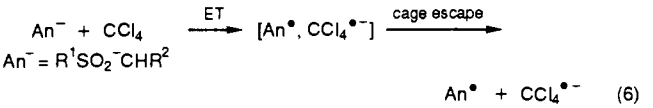
We confirmed these experiments, but because of the results described in section 2, we supplemented them by another set of experiments. The first experiment of the set was to check whether under the conditions of halogenation CCl_3^- would produce CCl_3 radicals in the presence of CCl_4 (reaction 4).

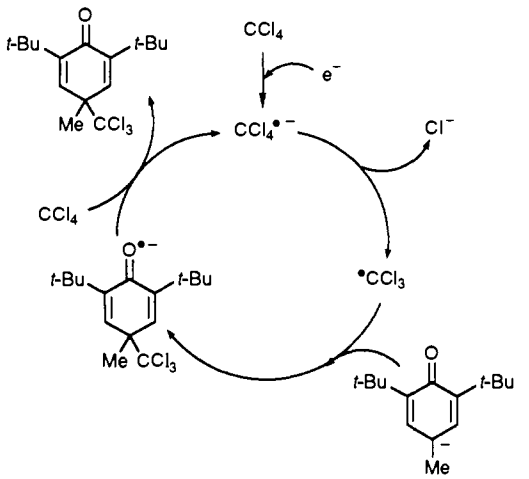
$$CCl_3^- + CCl_4 \rightarrow {}^{\bullet}CCl_3 + CCl_4^{\bullet -} \rightarrow 2CCl_3^{\bullet} + Cl^- \quad (4)$$

To do so, one adds BHT to the mixture of $HCCl_3$, CCl_4, *t*-BuOH, and KOH; the result of the experiment is trapping of $CCl_3^{\bullet}$ (and also $:CCl_2$) as in the halogenation reaction (reaction 5). In an unpublished work, C. Y. Meyers et al.[32] performed this experiment and reached the same conclusion.



One hypothesis that explains the trapping of $CCl_3^{\bullet}$ radicals during the halogenation reaction is the possibility of a chain reaction between $CCl_3^{\bullet}$ and BHT anion. This chain would be initiated by the CCl_4 radical anion that escaped from the cage, and it would magnify the presence of even tiny amounts of $CCl_3^{\bullet}$ (reaction 6).



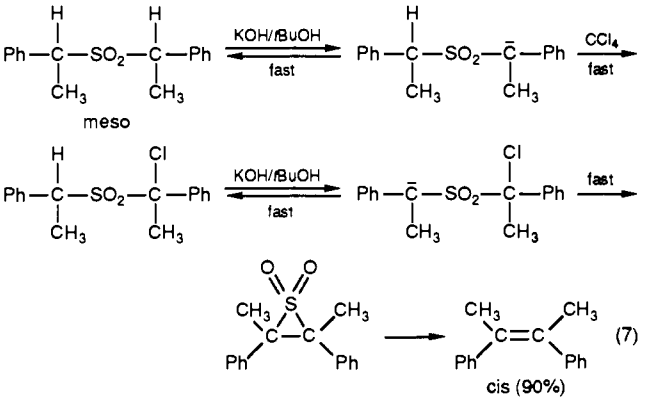


When radical chain inhibitors such as galvinoxyl or 2-methyl-2-nitrosopropane were added in reaction 5, the amount of **1** formed remained unchanged. This experiment does not support the intervention of a chain reaction like 6 in reaction 5.

Proof that the $CCl_3^{\bullet}$ trapped in reaction 2 may originate from the reaction of CCl_3^- with CCl_4 is not sufficient evidence to discard the RARP hypothesis. Part of the $CCl_3^{\bullet}$ trapped with BHT anion could originate from escape from the RARP and, part of it, from the reaction between CCl_3^- and CCl_4. On the other hand, proving that the CCl_3 radical may originate from two different sources considerably diminishes the weight of $CCl_3^{\bullet}$ trapping experiments as reasons for supporting the RARP hypothesis.

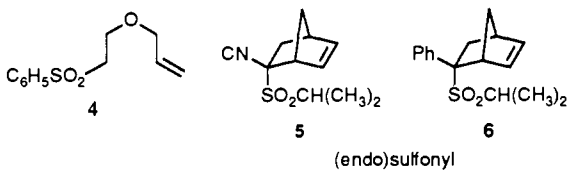
Therefore, one has to design less ambiguous experiments. Equation 2 *shows that, if CCl_3 radicals escape from the RARP, the sulfonyl radicals necessarily escape as well.* If they do so, it should be possible to observe them. This is the aim of the next section.

2. Experiments Aimed at Trapping Sulfonyl Radicals. Design of Free Radical Clocks. The first attempt at using the equivalent of free radical clocks was performed by C. Y. Meyers' group.[33] They studied the reaction of chlorination of *meso*-bis(α-methylbenzyl) sulfone with CCl_4, KOH, and tBuOH. This sulfone is chlorinated with retention of configuration (at least 90%), and the chlorinated product subsequently undergoes a Ramberg–Bäcklund reaction leading predominantly (90%) to the formation of *cis*-α,β-dimethylstilbene (reaction 7).[33a] The formation of 10% of *trans*-α,β-dimethylstilbene was rationalized by postulating a slow inversion–protonation of the carbanion precursor taking place concurrently with the halogenation of the carbanion by CCl_4.



Since α-sulfonyl carbanions maintain their configurational integrity and free sulfonyl radicals do not,[34] this experiment could be viewed as lending support to the nucleophilic attack of the sulfonyl carbanion on CCl_4. Because of six other reasons (among them, trapping of CCl_3 radicals). Meyers preferred to extract two other conclusions from this experiment: (i) α-sulfonyl radicals, if they are involved, are not free but caged, and (ii) since free α-sulfonyl radicals cannot be involved, this discards by the same token the possibility of a radical chain halogenation of sulfonyl carbanions.[29b]

There are known precedents of carbon-centered radicals partially maintaining their configurational integrity because they react rapidly inside a cage of solvent.[35] This experiment is crucial because configurational labeling corresponds to one of the fastest free radical clocks available (see, however, ref 35g for the limits of this statement). The 10% loss of configurational integrity, combined with the trapping of $CCl_3^{\bullet}$ in the medium, could suggest, however, that some of the intermediate species involved in the RARP (reaction 2) had escaped. Given our aim of finding substrates where ionic and radical pathways coexist, we synthesized radical clocks **4**, **5**, and **6** to study the frontier between ET and polar pathways of reactivity.



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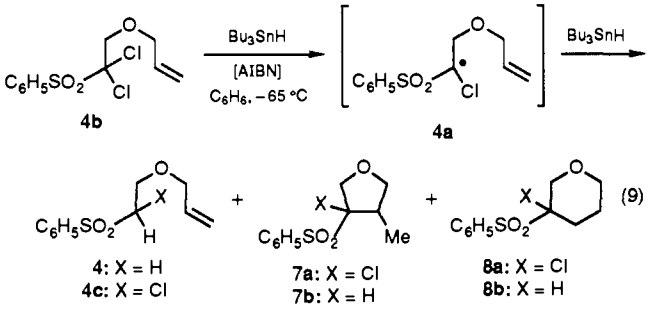
(35) (a) De Tar, D. F.; Weis, C. *J. Am. Chem. Soc.* **1957**, *79*, 3045. (b) Bartlett, P. D.; Pincock, R. E.; Rolston, J. H.; Schindel, W. G.; Singer, L. A. *J. Am. Chem. Soc.* **1965**, *87*, 2590. (c) Kopeck, K. R.; Gillan, T. *Can. J. Chem.* **1969**, *47*, 2371. (d) Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867. (e) Koenig, T.; Owens, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4054; **1973**, *95*, 8485. (f) Engström, J. P.; Greene, F. D. *J. Org. Chem.* **1972**, *37*, 968. (g) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5699.

Compound **4** was obtained through the following sequence of reactions:

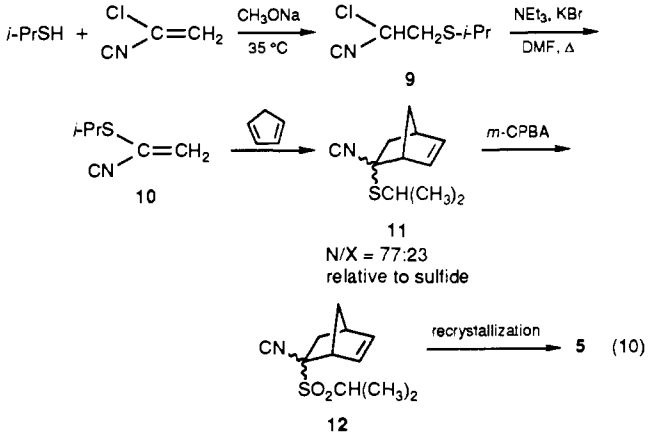
$$C_6H_5SO_2Na + BrCH_2CH_2OH \rightarrow C_6H_5SO_2CH_2CH_2OH \xrightarrow[NaOh,\ 50\%\ TBAB]{CH_2=CHCH_2Br} \mathbf{4} \quad (8)$$

The ability of **4** to behave as a free radical clock was checked by the set of reactions 9:

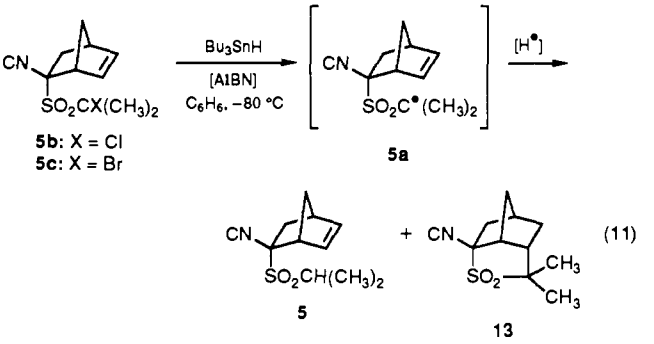


A series of competition reactions with increasing quantities of tri-*n*-butyltin hydride yielded a rough evaluation of the rate for intramolecular cyclization.[36] This rate should be around 1.8×10^6 s^{-1}. The precise rate could not be obtained because the α-electronic effect of SO_2 on the S_H2 rate of reaction of a carbon-centered radical is not known. The value 5×10^5 L M^{-1} s^{-1} adopted here for this rate takes into consideration that the effect of SO_2 on the stabilization of the carbon-centered radical should be weak. This proposition is supported by recent ab initio molecular orbital calculations where the stabilization brought on an α-carbocation, α-carbon-centered radical and α-carbanion by SO_2 are calculated to equal −29.4, +0.5, and −70.9 kcal mol^{-1}, respectively (stabilization for carbocations and carbanions, weak destabilization for the radicals).[37]

When substrate **4** was halogenated under Meyers' conditions (see the Experimental Section) using CCl_4, $BrCCl_3$, Br_2CCl_2, and C_2Cl_6 as halogenating agents, the observed products were only **4b** and **4c**. We found no trace (less than 1%) of the cyclized products that would have supported the involvement of radical species in these halogenations. This overall experimental result indicates that, if the RARP intermediate were involved in halogenation reaction 2, there would be no leak from the solvent cage. The result does not, however, eliminate the possiblity of an RARP in which the rate of intramolecular addition of the carbon-centered radical to the double bond is 100 times slower than an S_H2 reaction of this radical on the radical anion of CX_4. Therefore, faster radical clocks **5** and **6** were prepared (reaction 10) to obtain more information on this last point. α-Sulfonyl radicals **5a** derived

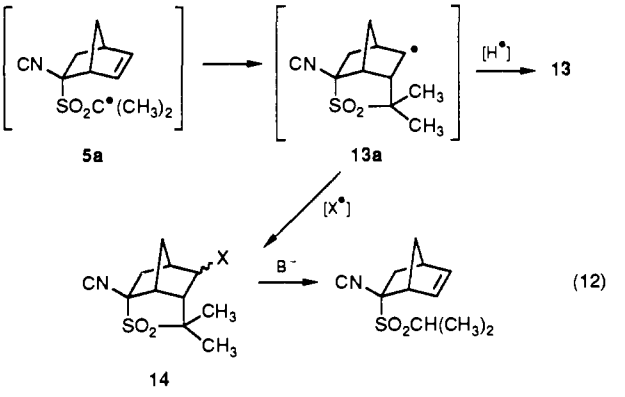


from **5** undergo a very rapid cyclization ($k \approx 2\ 10^8$ s^{-1}) when formed by the reaction of tributyltin hydride with **5c** (reaction 11) (see the Experimental Section). Sulfones **5** were then treated with the same various perhaloalkanes in KOH/*t*-BuOH. None of the experiments yielded a detectable amount of the cyclized product **13**.[38]



To validate the use of these free radical clocks to eliminate a radical intermediate, one has still to check a number of alternative possibilities that would disqualify the use of free radical clocks, even if no cyclized product **13** is found at the end of the halogenation reaction applied to substrates **5**. The first possiblity is that the intermediate radical **13a**, which has escaped from the RARP, prefers to abstract a halogen atom from the perhaloalkane rather than an H atom from *t*-BuOH (the rates of abstraction of H and Cl atoms by a carbon radical are quite similar, but Br atom abstraction is 10^4 times faster).[39] No trace of the halogeno tricyclic compound **14** has been detected, but **14** could also have returned to the starting carbanion by attack of a strong nucleophile on the halide function. However, **14** (X = Br) independently prepared, when submitted to the conditions where the halogenation by perhaloalkane is performed, does not undergo this kind of reaction.

A second possibility is that in reaction 12 the step **5a** → **13a** is partly reversible. Such reversibility has been shown to invalidate the use of free radical clocks.[40] This possibility was eliminated by submitting compound **15** to the reduction described by Barton.[41]



The tricyclic product **13** was obtained in a yield of 88%. No traces of **5** were detected. The presence of even small amounts of **5** would have suggested that the intermediate **13a** was in equilibrium with the uncyclized form **5a**.

A third possibility is that radical **13a**, rather than undergoing the β-scission that leads to **5a**, undergoes the β-scissions described in reaction 14.[42] This possibility was discarded by the careful study of the secondary products formed in reaction 13.

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(37) Clark, T. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus, K. D., Eds.; NATO ASI Series 197; Plenum Press: New York, 1990; p 14.
(38) Vacher, B.; Samat, A.; Chanon, M. *Tetrahedron Lett.* **1985**, *26*, 5129.
(39) (a) Fischer, H. *Radical Reaction Rates in Liquids*; Springer-Verlag: Berlin, 1984. (b) Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 2.
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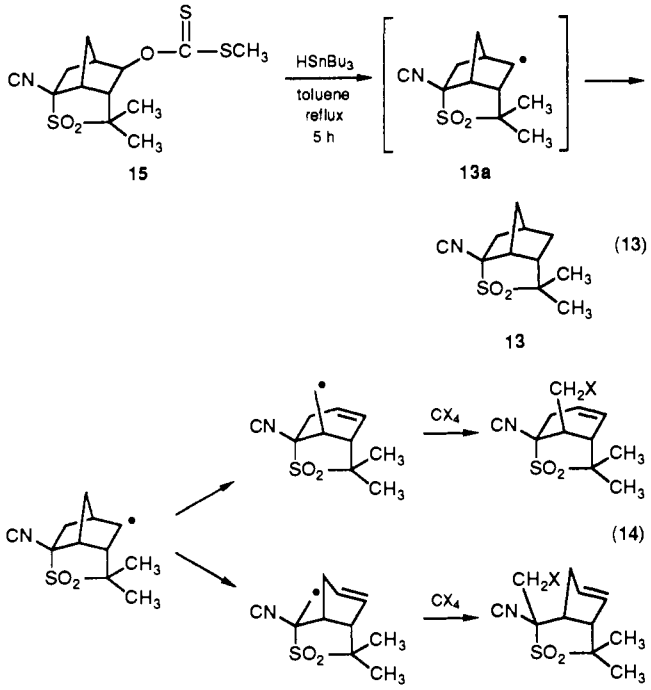
(41) Barton, D. H. R.; Ozbalik, N. In *Paramagnetic Organometallic Species in Activation, Selectivity, Catalysis*; Chanon, M., Julliard, M., Poite, J. C., Eds.; Kluwer Academic Publishers: Dordrecht, 1989; p 1.
(42) Beckwith, A. *Tetrahedron* **1981**, *37*, 3073.



The foregoing radical clock experiments therefore show that (a) very little if any radical escapes from the RARP and (b) even inside the cage, if this radical clock has a transitory existence, its intramolecular cyclization rate is still too slow to compete with the intermolecular S_H2 on a CX_4 radical anion (Scheme I). Contrary to alkyl halide radical anions, which are so labile that even their existence is dubious,[43] polyhalogenomethane radical anions are observed spectroscopically at low temperatures.[44]

No data are available on the reactivity of radical anions of perhaloalkanes in an S_H2 attack by a radical. The rate of reaction of their neutral counterpart in such an S_H2 reaction (reaction 15) is in the range of 10^2–10^3 L mol^{-1} s^{-1}.[45] Since the carbon–halogen

$$R^{\bullet} + Cl\text{–}CCl_3 \rightarrow RCl + {}^{\bullet}CCl_3 \qquad (15)$$

bonds in the radical anion are far weaker than in their neutral counterparts, one would expect an important acceleration of the S_H2 step, and therefore this step could reach or exceed the range of 10^9 s^{-1} evaluated for the intramolecular cyclization of **6**. This possibility of an extremely fast S_H2 attack on a radical anion places a limit on the value of the free radical clocks that we use here. The fastest free radical clock presently available is centered on the ring opening of (pentamethylcyclopropyl)carbinyl radical. This makes it possible to propose a very fast S_H2 ($k = 2 \times 10^{10}$ s^{-1}) reaction on a radical cation in the hydroxylation rebound mechanism of P-450.[35g] Unfortunately, these types of radical probes cannot be used in the present study because it is known that cyclopropylcarbinyl anions open very rapidly; therefore, in the present study the observation of ring-opened isomers would have no mechanistic significance. Even if the radical probes used in our study are among the fastest free radical clocks based on the formation of a C–C bond[46] rather than on C–C cleavage, they

Scheme I

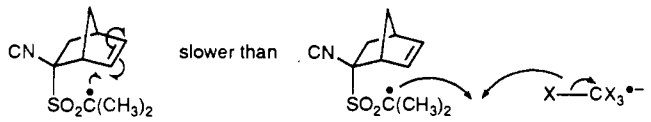


Table I. MNDO-SCF Calculations. Total Formation Energies of CCl_3^- and $CH_3SO_2CH_2^-$ Anions and Their Corresponding Radicals after Geometry Optimization (kcal mol^{-1})

anion	radical	ΔH (radical – anion)
CCl_3^-	CCl_3	
47.8	0.3	48.1
$CH_3SO_2CH_2^-$	$CH_3SO_2CH_2$	
92.9	155.4	62.5

should still be improved to reach the range of rate constants described in the literature.[35g] We are presently designing faster free radical clocks involving C–C bond formation with the guidance of a molecular mechanics program.

Two other experimental facts, however, point to the RARP hypothesis as a less likely possibility than the simple polar S_NCl^+ mechanism.[31] The first fact is the absence of any magnetic effect in reaction 1. Reaction 1 performed on compounds **5** and **6** in weak (2.1 T) or intense (17 T) magnetic fields did not yield even traces of cyclized products. Furthermore, no CIDNP effects could be observed during this reaction. The second experimental fact is the absence of temperature effect on the appearance of cyclized products in reaction 1 performed on substrate **5**. Indeed, even if the radical anions of polyhalogenomethanes are observed at low temperature,[44] they should still be highly dissociative at room temperature. If such is the case, by raising the temperature one should increase the participation of reaction 16 in the RARP. The

$$CCl_4^{\bullet -} \rightarrow {}^{\bullet}CCl_3 + Cl^- \qquad (16)$$

consequence of such a reaction would be the appearance of some coupling between the α-sulfonyl radical and $CCl_3^{\bullet}$ and/or the appearance of cyclized products in the final outcome of the reaction. None of these expectations was fulfilled when reaction 1 was performed on **5** at 60 °C in place of the usual conditions of halogenation by CX_4 (20 °C).

Furthermore, one of the referees pointed out that *N*-bromo imides (far stronger ET oxidants than polyhaloalkanes) also seem to transfer Br^+ to carbanions without the intervention of ET processes.[30b]

Therefore, all of the reported experimental data may be rationalized within a polar type displacement. At this point, we feel obliged to stick to the Occam's razor policy, which is followed by H. C. Brown in the classical vs non-classical carbocation dilemma, namely, as long as the observed facts can be explained within a classical approach, there is no compelling need to introduce a new theory.

That no measurable amounts of radicals **5a** escape from the RARP confirms the conclusion that the CCl_3 radicals trapped in the halogenation reaction originate only from reaction 4. We have to develop this point because it appeared first as a puzzle when we initiated this work. This is the aim of section 3.

3. Where Does the $CCl_3^{\bullet}$ Trapped with BHT Anion Come from? Theoretical Calculations and Thermodynamic Cycle. The correlation between the pK_a of the conjugate acids of carbanions and the ease of oxidation of these carbanions holds only for closely related carbanions.[47] Such a correlation cannot, therefore, be used to answer the following question: Why should the CCl_3 carbanion be a better reducing agent than the $R'SO_2CHR_2$ carbanion?

(43) (a) Compton, R. N.; Reinhart, P. W.; Cooper, C. C. *J. Chem. Phys.* **1978**, *68*, 4360. (b) Symons, M. C. R. *Pure Appl. Chem.* **1981**, *53*, 223. (c) Hotokka, M.; Roos, B. O.; Eberson, L. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1979. (d) Clark, T. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 203. (e) Mishra, S. P.; Symons, M. C. R. *Int. J. Radiat. Phys. Chem.* **1975**, *7*, 617. (f) Kevan, L. *Acc. Chem. Res.* **1981**, *14*, 138. (g) Ficksel, A. I.; Parman, V. N.; Zamaraev, K. I. *Chem. Phys.* **1982**, *69*, 135.

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The simplest answer could be that in the carbanions derived from polychloromethane compounds the negative charge on the carbon could be destabilized by Coulombic repulsion between the carbanionic charge and the lone pairs of electrons borne by the peripheric halogen substituents.[48] MNDO-SCF calculations[49] on the carbanion–radical equilibrium indeed suggest that ΔE (carbanion–radical) is greater for the perhalomethyl carbanion (Table I).

Furthermore, a referee pointed out that the SO_2R group has little capacity for stabilizing an adjacent radical by delocalizing the odd electron, whereas Cl stabilizes an adjacent radical. Thus, the BDE of the CH bonds in Ph_2CH_2 and Ph_2CHSO_2Ph are 82 and 87 kcal mol^{-1}, respectively, those in $PhCH_3$ and $PhCH_2SO_2Ph$ are 88 and 90 kcal mol^{-1}, respectively, and those in fluorene and 9-$PhSO_2$FlH are 80 and 82 kcal mol^{-1}, respectively. On the other hand, the BDE of 9-ClFlH is 2.6 kcal mol^{-1} lower than that of HFlH.[50]

Eberson and Ekström recently applied Marcus theory to rationalize the reactivity of polyhalogenated alkanes toward various donors.[51] The values of standard potentials $E°$ of CCl_4, $CBrCl_3$, and CBr_4 in DMF were taken as −0.60, −0.38, and −0.36, respectively (V vs NHE in DMF). These values may vary considerably from one solvent to another.[52] Recent cyclic voltammetry studies in THF for the monoelectronic oxidation of lithiated sulfones provide the only thermodynamic data presently available on α-sulfonyl carbanions. The $E°$ values of the carbanions formed from phenyl prenyl sulfone and phenyl benzyl sulfone are −0.28 and 0.14 V, respectively (vs NHE). However, even at 700 V s^{-1}, the oxidation wave is only slightly reversible, indicating that the half-life of the α-sulfonyl radical is only a few microseconds.[53]

$$R^1SO_2^-CHR^2 + CX_4 \rightarrow R^1SO_2C^{\bullet}HR^2 + CX_4^{\bullet -} \qquad \Delta G \quad (17)$$

Therefore, the ΔG associated with eq 17 should be slightly positive, and there is very little chance that structural modifications can lead to negative values beyond the threshold of −41.8 kJ mol^{-1} given by House as an indicator of relatively fast electron transfer.[11c] The direct measurement of $E°$ for CCl_3 anions is very difficult, and thermodynamic cycles[50] suggest a value of −0.39 ± 0.3 (vs NHE). Thus, the presently available $E°$ values do not provide a reliable answer to the question asked at the beginning of section 3.

Other possibilities may be proposed to explain the experimental results: carbon tetrachloride reacts with CCl_3 carbanions to yield CCl_3 radicals, whereas it reacts with α-sulfonyl carbanions to yield halogenation. Meyers et al. suggest that the possibility of escape of the radical from the solvent cage in an RARP increases with the stability of the radical.[29c] This stability could result either from thermodynamic considerations ($CCl_3^{\bullet}$ is more stabilized than $RSO_2C(CH_3)_2^{\bullet}$, contrary to what captodative[54] considerations would suggest) or kinetic considerations (CCl_3 radical is far less reactive than $RSO_2C(CH_3)_2^{\bullet}$ in the S_H2 attack on the radical anion of CCl_4). One referee suggested that the formation of $^{\bullet}CCl_3$ from $^-CCl_3$ and CCl_4 could be discussed in terms of a transient intermediate, $(Cl_3C\cdots Cl\cdots CCl_3)^-$, by analogy with what has been reported for perfluorinated compounds where entities such as $(R_F\cdots I\cdots R_F)^-$ exist as stable intermediates. Under such conditions, the electron transfer would have a strong inner sphere character and would therefore be strongly favored. Another possibility involves the role of spin orbit coupling[55] in thermal reactions where pairs of radical intermediates are postulated. We have suggested[56] the possibility of such a role in thermal reactions, where it has, until now, been studied mainly in photochemical reactions.[57] Under such a hypothesis, the CCl_3 radical substituted by three heavy substituents would promote a more efficient singlet–triplet transition within the RARP than the α-sulfonyl carbanion does; this would lead to an increased probability of cage escape for $^{\bullet}CCl_3$. More studies on polyhalogenated substrates must be designed to check these possibilities.

4. Consequences of This Work for $S_{RN}1$ Substitutions on Polyhalogenoalkanes. Several different groups have proposed that the chain reaction observed between nucleophiles and polyhalogenoalkanes[58] or substrates like bronidox[59] is initiated by an electron transfer between the nucleophile and the electrophilic substrate. Our results suggest that for some of these reactions a reasonable alternative to this mechanistic proposition could involve a different initiation step, such as the one shown in eq 18, provided that CY_3^- is a better reducing agent than Nu^-. The free radical clock methodology described in this report can be applied to these substrates, provided that the induced chain reactions are not too long.

$$Nu^- + X\text{–}CY_3 \rightarrow NuX + {}^-CY_3 \qquad (18)$$

$$^-CY_3 + X\text{–}CY_3 \rightarrow X\text{–}CY_3^{\bullet -} + {}^{\bullet}CY_3$$

$$^{\bullet}CY_3 + X\text{–}CY_3 \rightarrow \text{triggering of a chain by } S_H2$$

Experimental Section

General Considerations. Tetrahydrofuran was distilled from a purple solution of sodium/benzophenone prior to use. Commercial-use (anhydrous grade) benzene was stored over 4-Å or 3-Å molecular sieves. Toluene was distilled over sodium and stored over 4-Å molecular sieves. Gas chromatography–mass spectroscopy was performed on a Ribermag R 10 (10 C; vector gas, helium; V = 70 eV; working temperatures, injector 300 °C, interface 300 °C, source 150 °C). Column chromatography was performed on Merck 60 silica gel (70–230 mesh). Gas chromatography was performed on an Intersmat IGC 121 FL apparatus connected to an Intersmat ICR 1B integrator. Preparative gas chromatography was performed on a Varian Aerograph A 700 chromatograph. ^1H (100 MHz) and ^{13}C (25 MHz) NMR spectra were recorded on a Bruker AC 100, a Bruker AM 200 (^1H, 200 MHz; ^{13}C, 50 MHz), and a Bruker AM 400 X (^1H, 400 MHz; ^{13}C, 100 MHz).

1. Trapping of CCl_3 Radicals with 2,6-Di-*tert*-butyl-4-methylphenoxide (BHT). To a typical halogenation mixture made of CCl_4 (10 mL), *t*-BuOH (10 mL), and benzyl phenyl sulfone (10 mL, 1 g, 4.3 mmol) was added BHT (2.2 g, 10 mmol). The solution was degassed and stirred at 20 °C under nitrogen atmosphere. Powdered KOH (2.0 g) was added. At the end of the reaction, the solution was poured into cold water and decanted. The aqueous phase was acidified with HNO_3 and extracted with Et_2O. The organic phases were washed with water, dried with $MgSO_4$, and concentrated under vacuum. A gas chromatography–mass

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spectrometry analysis, compared with the authentic samples, revealed the presence of compounds **1–3**. Mass spectrometry data (column: CPSIL 5, 50 m; temperature range, 80–280 °C, 5 °C min^{-1}): **1**, M = 336, *m/e* (relative intensity) 303 (0.7), 301 (0.9), 219 (31.2), 57 (100), 41 (42.9); **2**, M = 302, *m/e* (relative intensity) 304 (0.6), 302 (1.1), 269 (2.0), 267 (7.8), 219 (23.9), 57 (100), 41 (39.7); **3**, unidentified product.

Authentic samples of compounds **1–3** were prepared from an experiment like the one described below (see 2.1b) followed by a preparative gas chromatography separation (column: SE 30, 30%, ϕ, $^3/_8$ in.; length, 1.50 m; 160 °C): **1**, ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.25 (s, 18 H), 1.64 (s, 3 H), 6.75 (s, 2 H); **2**, ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.25 (s, 18 H), 1.43 (s, 3 H), 5.63 (s, 2 H), 6.55 (s, 1 H); **3**, unidentified product.

2. Origin of Compounds 1–3. In all of the described experiments, the qualitative and quantitative analyses were performed by gas chromatography by comparison with authentic samples (column: SE 30, 10%, 2 m; temperature range, 80–280 °C, 10 °C min^{-1}).

2.1. Evidence for ET between the CCl_3^- Anion and CCl_4. (a) The contents of a flask containing CCl_4 (10 mL), $HCCl_3$ (2.5 mL, 30.1 mmol), BHT (3.5 g, 15.9 mmol), and TEBA (triethylbenzylammonium chloride, 0.5 g, 1.5 mmol) were vigorously stirred, while a 50% solution of KOH (50 mL) was added. After 4 h of reaction, the organic layer was collected. The aqueous phase was acidified with HNO_3 and extracted with Et_2O. The organic phases were washed with water and dried on $MgSO_4$ (unreacted BHT, 69%; yield, %: **1**, 0.14; **2**, 0.12; **3**, 5).

(b) To a reaction mixture containing CCl_4 (5 mL), dioxane (5 mL), $HCCl_3$ (2.5 mL, 30.1 mmol), and BHT (7.0 g, 31.8 mmol) was added NaH (0.7 g, 29.2 mmol). The solution was stirred for 4 h (unreacted BHT, 90%; yield, %: **1**, 1; **2**, 5; **3**, 4).

2.2. Origin of Compounds 2 and 3: Trapping of Dichlorocarbene. Into a mixture containing dioxane (5 mL), $HCCl_3$ (2.5 mL), and BHT (7 g) was added (a) 0.7 g of NaH (unreacted BHT, 75%; yield, %: **2**, 17; **3**, 8) or (b) 1 g of powdered KOH (unreacted BHT, 93%; yield, %: **2**, 5; **3**, 2). Furthermore, we have verified that, in the absence of $HCCl_3$, experiments a and b do not lead to the formation of products **1–3**.

2.3. 1 Comes from Trapping of CCl_3 Radical. The mixture of dioxane (2.5 mL), CCl_4 (2.5 mL), and BHT (0.5 g) was irradiated for 5 h (UV lamp, Hg pressure, 400 W). Only **1** was identified as a product of this reaction (BHT, 89%; yield, %: **1**, 11). It has been verified that **1** is stable in the dioxane (or *t*-BuOH)/CCl_4/KOH medium.

2.4. Turnover of the Supposed Chain Reaction of CCl_3 Radical with BHT. The turnover (t.o.) of the chain (reaction 6) can be expressed as the ratio of the number of molecules of **1** formed to the number of CCl_3 radicals generated by the halogenation reaction. Reactions a–c would describe this chain:

$$R^1SO_2CHR^2 \xrightarrow{2CCl_4} R^1SO_2CCl_2R^2 + 2CCl_3^- \quad \text{(a)}$$

$$CCl_3^- \xrightarrow[CCl_4]{ET} 2CCl_3^{\bullet} \xrightarrow[\text{chain reaction (reaction 6)}]{BHT/CCl_4} \mathbf{1} \quad \text{(b)}$$

$CCl_3^- \rightarrow$

$Cl^- + :CCl_2$, the dichlorocarbene then yields **2** + **3** + ϵC_2Cl_4 (c)

Formed [$^{\bullet}CCl_3$] = 4[$R^1SO_2CH_2R^2$] − ([**2**] + [**3**] + ϵC_2Cl_4) and t.o. = [**1**]/[$^{\bullet}CCl_3$].

In a constant experimental medium, (*t*-BuOH (5 mL), CCl_4 (5 mL), BHT (0.106 g, 0.48 mmol)) two experiments were performed with 0.25 g (1.1 mmol) and 0.025 g (0.11 mmol) of sulfone **4**, respectively. Powdered KOH was added (1 g), and the mixture was kept at 25 °C and treated at the end of the reaction in the usual manner. The data obtained for these two experiments were as follows ([**1**], [**2** + **3**], t.o., respectively): exp 1, 1.3×10^{-4} mol, 6.35×10^{-5} mol, 0.03; exp 2, 4.4×10^{-5} mol, 5.3×10^{-5} mol, 0.11.

2.5. Trapping of CCl_3 Radicals with BHT in the Presence of Other Radical Traps. In a constant experimental medium (*t*-BuOH (5 mL), CCl_4 (5 mL), sulfone **4** (0.25 g, 1.1 mmol), and BHT (0.1 g, 0.45 mmol)) was added galvinoxyl (0.05 g, 0.11 mmol) or 2-methyl-2-nitrosopropane (0.02 g, 0.11 mmol). After the addition of KOH (1 g) and the usual treatments and analysis, the measured ratios [**1**]/[**BHT**] were 0.040 and 0.060, respectively. Without the addition of radical traps other than BHT, this ratio was 0.080.

3. Evaluation of the Oxidation Potential of CCl_3 Anion. From the thermochemical cycles involving carbanion oxidation potentials and following the recent Parker et al. conventions:[50d]

$HCCl_3(s) \rightleftharpoons CCl_3^-(sol) + e$	$2.30RTpK_a$
$CCl_3^-(sol) \rightleftharpoons CCl_3^{\bullet}(sol) + e$	$-FE^\circ_{ox}$ (CCl_3^-, sol)
$H^+(sol) \rightleftharpoons 0.5H_2(g)$	$\Delta G^\circ_f(H^{\bullet}, gas)$
$H^{\bullet}(g) \rightleftharpoons H^{\bullet}(sol)$	$\Delta G^\circ_{sol}(H^{\bullet}, sol)$
$HCCl_3 \rightleftharpoons CCl_3^{\bullet}(sol) + H^{\bullet}(sol)$	BDE

where BDE = 2.3 $pK_a + F[E_{ox}(CCl_3^-, sol) - E^\circ(H^+, sol)] + \Delta G^\circ_f(H^{\bullet},g) + \Delta G^\circ_{sol}(H^{\bullet}, sol)$, and

$$H^+(aq) + e \rightleftharpoons 0.5H_2(g)$$

$$H^+(sol) \rightleftharpoons H^+(aq)$$

where BDE = $2.3RTpK_a + FE^\circ_{ox}(CCl_3^-, sol) + C$. With BDE = 400.4 kJ mol^{-1}, pK_a = 17, and C = 265.3 kJ mol^{-1}, one obtains $E^\circ_{ox}(CCl_3^-, sol)$ = +0.39 V versus NHE in DMSO.

2-(Phenylsulfonyl)ethanol. Commercially available sodium sulfinate (55 g, 0.335 mol) and tetrabutylammonium bromide (35 g, 0.1 mol) were dissolved in water (200 mL). 2-Bromoethanol (35 g, 0.25 mol) in 250 mL of CH_2Cl_2 was added. The mixture, vigorously stirred, was refluxed for 20 h. The solution was decanted, and the aqueous layer was extracted three times with benzene. The organic layers were concentrated. The alcohol was distilled under vacuum, 33 g (65% yield): bp 150–160 °C (1 mmHg); ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.40 (t, 2 H), 3.92 (t, 2 H), 7.40–8.20 (m, 5 H).

2-(Allyloxy)ethyl Phenyl Sulfone (4). Tetrabutylammonium bicarbonate (0.039 g, 0.13 mmol) was dissolved in a 50% sodium hydroxide solution (10 mL). Allyl bromide (7 mL) and 2-(phenylsulfonyl)ethanol (0.5 g, 2.6 mmol) were added. The mixture was vigorously stirred at 20 °C for 6 h. After decantation, the aqueous layer was extracted three times with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and concentrated under vacuum (1 mmHg) to eliminate excess allyl bromide. The crude product, an oil, was purified by silica gel chromatography with chloroform as eluent, 0.047 g (81% yield): ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.39 (t, 2 H), 3.73 (t, 2 H), 3.80 (d, 2 H), 5.0 (m, 1 H), 5.68 (m, 2 H), 7.46 (m, 3 H), 7.83 (m, 2 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 56.1, 63.3, 71.6, 117.0, 127.9, 129.1, 133.6, 133.9, 133.9. Anal. Calcd for $C_{11}H_{14}SO_3$: C, 58.38; H, 6.24; S, 14.17. Found: C, 58.43; H, 6.33; S, 14.10.

1,1-Dichloro-2-(allyloxy)ethyl Phenyl Sulfone (4b). The sulfone **4** (0.5 g, 2.2 mmol) was dissolved in *t*-BuOH (5 mL) and CCl_4 (5 mL). The solution was degassed with argon, and KOH (1 g) was added. The reaction was performed under argon atmosphere at 20 °C for 6 h. Cold water (10 mL) and then concentrated HNO_3 were added until an acidic pH was reached. After decantation, the aqueous layer was washed three times with Et_2O. The organic layers were dried ($MgSO_4$) and concentrated under vacuum. The crude product was purified by liquid chromatography on silica gel ($CHCl_3$ as eluent), 0.6 g (92% yield): ^{1}H NMR (100 MHz, $CDCl_3$) δ 4.15 (d, 2 H), 4.17 (s, 2 H), 5.26 (m, 1 H), 5.84 (m, 2 H), 7.62 (m, 3 H), 8.03 (m, 2 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 67.7, 73.4, 74.2, 118.5, 128.5, 132.1, 133.2, 135.0, 135.2. Anal. Calcd for $C_{11}H_{12}SO_3Cl_2$: C, 44.75; H, 4.10; S, 10.86; Cl, 24.02. Found: C, 44.80; H, 4.07; S, 10.81; Cl, 24.10.

Evaluation of the Cyclization Rate of the Radical 4a. The dichloro sulfone **4b** (0.5 g, 1.7 mmol) was dissolved in dry benzene (10 mL). The stirred solution was degassed under argon and heated at 65 °C. *n*-Bu_3SnH and a few crystals of 2,2′-azobisisobutyronitrile (AIBN) were added. The temperature was kept at 65 °C for 12 h. At the end, CH_3CN (15 mL) was added. The solution was washed several times with hexane and concentrated under reduced pressure. The analysis of the mixture was performed by GPC/MS coupling (electronic impact and chemical ionization with CH_4; column: SE 30, 50 m; temperature range, 100–300 °C, 4 °C min^{-1}). Two experiments were performed with 1.2 and 5 equiv of *n*-Bu_3SnH/**4b**. The ratios of **7a**, **8a**, **7b** + **8b**, **4** + **4c**, and **4b** are given, respectively: exp 1 39.7, 20.2, 0, 23.3, 12.8; exp 2 18.1, 14.0, 12.1, 46.0, 5.0. The rate of H abstraction from *n*-Bu_3SnH by a carbon-centered radical was taken as 3.25×10^6 mol^{-1} s^{-1}.[39] This value leads to a cyclization rate of **4a** equal to 1.8×10^6 s^{-1}.

2-Chloro-2-cyanoethyl Isopropyl Sulfide (9), 1-Cyano-1-(isopropylthio)ethylene (10), and 5-*endo*-(Isopropylthio)-5-*exo*-cyano-2-norbornene (11). The synthesis and physical and NMR characteristics of these compounds have been described by L. Stella et al.[60]

5-*endo*-(Isopropylsulfonyl)-5-*exo*-cyano-2-norbornene (5). *m*-Chloroperbenzoic acid (1.8 g, 10.4 mmol) was dissolved in cold CH_2Cl_2 (40 mL, 0–5 °C). This solution was added dropwise to a solution of norbornene **11** (1 g, 5.2 mmol; *endo*-sulfide/*exo*-sulfide = 77:23) in cold CH_2Cl_2 (20 mL, −60 °C, acetone/liquid nitrogen bath). At the end of the addition, the cold solution was filtered off and washed three times with a 5% solution of aqueous NaOH and then three times with water. After drying ($MgSO_4$), CH_2Cl_2 was evaporated under reduced pressure. The crude product obtained as an oil crystallized on standing, 0.80 g (68%). The exo and endo isomers were separated by a chromatography on silica gel using a benzene/ethyl acetate mixture (93:7) as eluent. The

(60) Boucher, J. L.; Stella, L. *Tetrahedron* **1985**, *41*, 875.

endo isomer was then recrystallized from a hexane/diethyl ether mixture: mp 63–64 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.41 (d, J = 6.9 Hz, 3 H), 1.45 (d, J = 6.9 Hz, 3 H), 1.71 (ddt, J = 9.1, 2.7, 1.5 Hz, 1 H), 1.81 (d, J = 9.1 Hz, 1 H), 2.08 (dd, J = 12.6, 2.7 Hz, 1 H), 2.47 (dd, J = 12.6, 2.7 Hz, 1 H), 3.20 (s, 1 H), 3.74 (s, 1 H), 3.76 (hept, 1 H), 6.13 (dd, J = 5.6, 2.9 Hz, 1 H), 6.36 (dd, J = 5.6, 3.1 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.6, 16.6, 39.1, 43.5, 49.3, 53.8, 53.9, 63.8, 120.1, 130.7, 139.3. 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.

5-*endo*-[(1-Chloro-1-methylethyl)sulfonyl]-5-*exo*-cyano-2-norbornene (5b). This compound was prepared by a phase transfer catalyzed reaction from the sulfone **5**. Aqueous phase: 50% sodium hydroxide solution (10 mL) and tetra-*n*-butylammonium bromide (0.071 g, 0.22 mmol). Organic phase: CCl_4 (10 mL) and sulfone **5** (0.5 g, 2.2 mmol). The mixture was vigorously stirred at 20 °C for 6 h. At the end of the reaction, the organic layer was decanted, and the aqueous phase was extracted with CH_2Cl_2 (20 mL). The organic layers were washed two times with water (10 mL), dried ($MgSO_4$), and concentrated under vacuum. The crude product was dissolved in benzene and chromatographed on silica gel (benzene as eluent). The solvent was evaporated under reduced pressure. The pure chloro compound **5b** crystallized on standing, 0.41 g (71%): mp 45–46 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.72 (ddt, J = 9.7, 2.8, 1.7 Hz, 1 H), 1.89 (d, J = 9.7 Hz, 1 H), 2.03 (s, 3 H), 2.18 (s, 3 H), 2.20 (dd, J = 13.1, 2.8 Hz, 1 H), 2.62 (dd, J = 13.1, 3.7 Hz, 1 H), 3.20 (s wide, 1 H), 3.85 (s, wide, 1 H), 6.13 (dd, J = 5.5, 2.74 Hz, 1 H), 6.38 (dd, J = 5.5, 3.2 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) 28.3, 29.1, 40.6, 43.2, 49.2, 54.9, 63.9, 85.3, 120.1, 130.7, 139.4. 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.

5-*endo*-[(1-Chloro-1-methylethyl)sulfonyl]-5-*exo*-phenyl-2-norbornene (6b). *n*-Butyllithium (1.5 mL of a 1.6 M solution in hexane, 2.35 mmol) was added dropwise to a well-stirred solution of *endo*-sulfone **6** (0.65 g, 2.35 mmol) in THF (10 mL) at −70 °C. A solution of C_2Cl_6 (1.7 g, 7.17 mmol) in THF (15 mL) was then added dropwise. After 2 h of stirring, the mixture was allowed to return to room temperature. The solution was diluted with Et_2O and acidified with HNO_3 (0.1 M), and the aqueous layer was extracted with Et_2O. The organic layers were washed with water, dried over $MgSO_4$, and evaporated under reduced pressure. The excess of C_2Cl_6 was removed on a rotary evaporator at 50 °C/1.5 mmHg to yield the white crystalline halogenated sulfone. The sulfone was washed with pentane, 0.643 g (88%): mp 71–72 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.41 (dd, J = 5.7, 3.0 Hz, 1 H), 6.35 (dd, J = 5.7, 2.8 Hz, 1 H), 4.01 (s wide, 1 H), 3.03 (s wide, 1 H), 3.39 (dd, J = 13.1, 2.9 Hz, 1 H), 2.91 (dd, J = 13.1, 4.0 Hz, 1 H), 1.51 (s, 3 H), 1.40 (ddt, J = 8.7, 2.9, 1.7 Hz, 2 H), 1.18 (d, J = 8.7 Hz, 1 H), 1.02 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) 139.0, 137.7, 132.8, 131.6, 130.1, 128.6, 128.3, 84.8, 79.2, 55.2, 48.3, 43.5, 37.5, 28.2. 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-Cyano-6,6-dimethyl-3,8-methano-7-thiabicyclo[3.2.1]octane 7,7-Dioxide (13). Into a solution of chloro sulfone **5b** (0.333 g, 1.28 mmol) in dry, degassed benzene (10 mL) containing few crystals of AIBN was added *n*-Bu_3SnH (1.92 mmol). The solution was refluxed for 24 h under a nitrogen atmosphere. After the solvent was removed, the residue was dissolved in CH_3CN (10 mL). The solution was washed with dry hexane (3 × 10 mL) and evaporated to yield the desired tricyclic compound **13** free of tin residue, 0.188 g (65%). The crude product was recrystallized in ethanol: mp 138–139 °C; ^{1}H NMR (200 MHz, $CDCl_3$) (attributions are not complete: correlations ^{13}C–^{1}H and ^{1}H–^{1}H are necessary to obtain a full attribution)[61] δ 1.42 (s, 3 H), 1.44 (m, 1 H), 1.50 (s, 3 H), 1.69–1.94 (m, 3 H), 2.23 (dt, 1 H), 2.40 (dt, 1 H), 2.47–2.59 (m, 2 H), 3.27 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) 20.9, 25.9, 29.1, 36.4, 39.9, 42.5, 48.4, 49.6, 62.7, 63.2, 116.6. 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.

Evaluation of the Cyclization Rate of the Radicals 5a and 6a (Precursor is 6). The procedure is the one described for **4a**, using increasing quantities of *n*-Bu_3SnH. For *n*-Bu_3SnH/**5b** ratios of 2.5, 10 and 50, the ratios **13**/**5** were 100:0, 93:7, and 60:40, respectively. These data were obtained by HPLC analysis (Si 60, 7 μm column, $CHCl_3$ as eluent). The rate of H abstraction from *n*-Bu_3SnH by a carbon-centered radical was taken as 3.25 10^6 L mol^{-1} s^{-1}.[39] For cyclizations with high rate constants, the nitroxide radical trapping method[35g] would be more appropriate, and we plan to apply it to these cyclizable probes.

For *n*-Bu_3SnH/**6b** ratios of 20, 50, and 100, the ratios of cyclized product/**6** were >99:1, 97:3, and 93:7, respectively. These data were determined on the crude product from high-resolution ^{1}H NMR analysis.

5-*endo*-(Isopropylsulfonyl)-5-*exo*-cyano-2,3-*exo*-epoxynorbornane (16). Sulfide **11** (0.209 g, 1.08 mmol of a mixture of endo/exo isomers) was dissolved in 10 mL of acetic acid. Hydrogen peroxide (4 mL, 40 mmol of a 30% solution in water) was added, and the mixture was stirred for 103 h at room temperature. The mixture was diluted with water (20 mL) and extracted with three portions of CH_2Cl_2 (10 mL). The combined organic extracts were washed three times with saturated aqueous $NaHCO_3$ and water. Drying over $MgSO_4$ was followed by evaporation of the solvent to yield a white solid. A single recrystallization (ethyl acetate/hexanes) provided pure epoxide, 0.107 g (41%): mp 118–120 °C; ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.74 (sept, J = 6.8 Hz, 1 H), 3.67 (dm, J = 3.6 Hz, 1 H), 3.40 (s large, 1 H), 3.33 (dm, J = 3.4 Hz, 1 H), 2.84 (s large, 1 H), 2.31 (m, 2 H), 1.84 (dm, J = 11.5 Hz, 1 H), 1.52 (d, J = 6.8 Hz, 3 H), 1.48 (d, J = 6.8 Hz, 3 H), 1.36 (dm, J = 11.1 Hz, 1 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 118.6, 65.3, 54.3, 49.4, 48.7, 47.1, 37.7, 37.0, 26.5, 16.6, 14.3. Anal. Calcd for $C_{11}H_{17}NO_3S$: C, 54.77; H, 6.22; N, 5.81; S, 13.3. Found: C, 54.77; H, 6.20; N, 5.79; S, 13.2.

1-Cyano-6,6-dimethyl-4-*exo*-hydroxy-3,8-methano-7-thiabicyclo-[3.2.1]octane 7,7-Dioxide (17). Epoxide **16** (0.875 g, 3.63 mmol) was added to an oven-dried round-bottomed flask and dissolved in dry THF (10 mL). The resulting solution was brought under a nitrogen atmosphere and cooled to −78 °C. At that temperature, *n*-BuLi (2.3 mL of a 1.6 M solution in hexanes, 3.63 mmol) was added by syringe, and the resulting mixture was stirred for 30 min at a temperature range of −78 to −50 °C before being recooled to −78 °C. At that temperature, $BF_3{\cdot}OEt_2$ (0.9 mL, 7.26 mmol) was added, and the reaction mixture was stirred for 30 min at −60 °C and allowed to warm to −20 °C. After cooling (−78 °C), the reaction mixture was quenched with saturated aqueous $NaHCO_3$. After the solution was warmed to room temperature, water (20 mL) was added and the product was extracted with $CHCl_3$. The combined organic extracts were dried over $MgSO_4$ and concentrated to yield a white solid. Recrystallization of the product from $CHCl_3$ yielded alcohol as white crystals, 0.525 g (60%): mp 156–158 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 3.70 (m, 1 H), 3.30 (m, 2 H), 2.28 (ddd, J = 14.2, 2.4, 1.3 Hz, 1 H), 2.23 (dd, J = 14.2, 3.5 Hz, 1 H), 2.19 (m, 1 H), 2.16 (dq, J = 11.2, 1.7 Hz, 1 H), 1.79 (dq, J = 11.2, 1.55, 1 H), 1.48 (s, 3 H), 1.47 (s, 3 H); ^{13}C NMR (100 MHz, CD_3OD) 117.8, 73.4, 63.6, 61.2, 49.5, 45.1, 39.0, 36.9, 26.2, 20.7. Anal. Calcd for $C_{11}H_{17}NO_3S$: C, 54.48; H, 6.22; N, 5.80. Found: C, 54.57; H, 6.14; N, 5.60.

1-Cyano-6,6-dimethyl-3,8-methano-4-*exo*-[(methylthio)thioxomethoxy]-7-thiabicyclo[3.2.1]octane 7,7-Dioxide (15). A slurry of freshly washed (benzene) sodium hydride (0.030 g of a 55–60% oil mixture, 1.26 mmol), dry THF (3 mL), alcohol **17** (1.507 g, 6.25 mmol) in dry THF (2.2 mL), and imidazole (0.0028 g) was refluxed under nitrogen for 3 h followed by the addition of carbon disulfide (0.2 mL, 3.32 mmol) in one portion. The solution was warmed under reflux for 30 min followed by the addition of methyl iodide (0.2 mL, 3.21 mmol) in one portion. The mixture was warmed under reflux for 30 min, cooled to room temperature, and partitioned between 15 mL of CH_2Cl_2 and 15 mL of water. The organic phase was dried ($MgSO_4$), and the solvent was evaporated. The resulting residue was chromatographed on silica gel (elution with toluene, 5% ethyl acetate in toluene, and 10% ethyl acetate in toluene) to yield xanthate as a white solid, 1.262 g (61%): mp 177–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (m, 1 H), 3.34 (dq, J = 4.3, 1.5 Hz, 1 H), 2.8 (m, 1 H), 2.55 (s, 3 H), 2.54–2.57 (m, 1 H), 2.49 (dd, J = 14.7, 2.7 Hz, 1 H), 2.30 (dd, J = 14.7, 4.2 Hz, 1 H), 2.11 (ddt, J = 11.4, 2.7, 1.4 Hz, 1 H), 1.91 (dq, J = 11.5, 1.6 Hz, 1 H), 1.53 (s, 3 H), 1.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 116.0, 82.6, 62.3, 62.0, 56.9, 48.2, 41.6, 37.4, 36.7, 25.9, 21.2, 19.5. Anal. Calcd for $C_{13}H_{17}NO_3S_3$: C, 47.13; H, 5.14; N, 4.23. Found: C, 46.40; H, 5.31; N, 3.89.

Reduction of Xanthate 15. Xanthate **15** (0.035 g, 0.12 mmol) dissolved in dry toluene (2 mL) was added to *n*-Bu_3SnH (0.047 mL, 0.17 mmol) in dry, degassed toluene (1 mL) warmed under reflux. The solution was warmed under reflux for an additional 5 h under nitrogen, cooled, and concentrated. CH_3CN was added (12 mL) to the residue, and the mixture was washed five times with hexane. Evaporation of the solvent yielded the tricyclic product **13** as a white solid (0.023 g, 88%), the spectroscopic properties of which were identical with those reported in the literature.[61]

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Picoche for his help on this occasion.

Registry No. 4, 140438-20-6; **4a**, 140438-22-8; **4b**, 140438-21-7; **4c**, 140438-27-3; **5a**, 140438-30-8; **5b**, 134359-20-9; *exo*-**5**, 136266-08-5; *endo*-**5**, 134359-22-1; **6a**, 140438-31-9; **6b**, 140438-29-5; *endo*-**6**, 140438-28-4; **7a**, 140438-23-9; **7b**, 140438-25-1; **8a**, 140438-24-0; **8b**, 140438-26-2; *exo*-**11**, 108384-32-3; *endo*-**11**, 108384-28-7; **13**, 111740-30-8; **15**, 140438-34-2; **16**, 140438-32-0; **17**, 140438-33-1; BHT, 128-37-0; $CCl_3^{\bullet}$, 3170-80-7; CCl_3^-, 14478-07-0; CCl_4, 56-23-5; $H_2C{=}CHCH_2Br$, 106-95-6; $HO(CH_2)_2SO_2Ph$, 20611-21-6.

Antenna-Initiated Photochemistry of Distal Groups in Polyfunctional Steroids. Intramolecular Singlet and Triplet Energy Transfer in 3α-(Dimethylphenylsiloxy)-5α-androstan-17-one and 3α-(Dimethylphenylsiloxy)-5α-androstane-11,17-dione[1,2]

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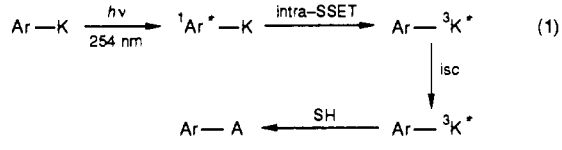
Abstract: Photolysis of 3α-(dimethylphenylsiloxy)-5α-androstane-11,17-dione (**1**) in acetonitrile with triethylamine, using 266-nm light absorbed by the dimethylphenylsiloxy (DPS) chromophore, leads to reduction of the C17 keto group as the principal photoreaction. This contrasts with the direct photolysis of the ketone moieties with 308-nm light, wherein epimerization of ring D is the major consequence and reduction is minimal. Triplet quenching studies with *cis*-1,3-pentadiene confirm that the reduction is derived from the C17 keto triplet state, while the epimerization originates with the C17 excited singlet state. Photolysis of 3α-(dimethylphenylsiloxy)-5α-androstan-17-one (**3**) under similar conditions gives qualitatively similar results but with a higher fraction of its epimer using 266-nm light and complete absence of reduction upon direct ketone excitation. Intramolecular singlet/singlet energy transfer (intra-SSET) from the DPS antenna to the carbonyl groups is demonstrable in both substrates by the reduced fluorescence quantum efficiencies and singlet lifetimes of the DPS group in these steroids. The rates of energy migration are ca. 2×10^8 and 29×10^8 s^{-1} for **3** and **1**, respectively, reflecting the greater efficiency of transfer to the more proximal C11 keto group. Intramolecular triplet/triplet energy transfer (intra-TTET) is also evidenced in **3**, for example, by the triplet-derived reduction chemistry at C17 which is uniquely characteristic of the antenna excitation; a through-bond exchange mechanism is proposed. Additional triplet chemistry observed at C17 in the diketone, **1**, is rationalized by a conversion from the singlet to the triplet manifold at the C11 ketone (i.e., C11 acts as a singlet/triplet switch) followed by triplet energy migration from C11 to C17.

As part of our general interest in the photochemistry of polyfunctional molecules and mechanisms for delocalizing and transmitting electronic excitation, we have been exploring the use of antenna chromophores to "harvest" photon energy which can then be utilized to selectively activate functioinalities distal to the site of initial excitation.[3] Our prototypical system has been the aryl/ketone functional group pair, where we have demonstrated aryl-initiated photoreduction of the carbonyl group via intramolecular singlet/singlet energy transfer (intra-SSET);[4,5] cf. eq 1 wherein Ar---K and Ar---A are the aryl ketone and product aryl alcohol, respectively.



The mechanism by which intra-SSET occurs in aryl ketones has been a subject of considerable recent interest.[6-11] There is evidence that through-bond interactions (TBI) involving bridging C–C σ bonds play a role in energy migration,[6b,8,9,11] and examples involving naphthalene/ketone pairs separated by extended, rigid C–C bridges, wherein the rates of intra-SSET are strongly dependent on the length and configuration of the C–C bridges, are taken as indicative of TBI intra-SSET primarily through an exchange mechanism.[6b,11]

Superimposed on the photophysical interest is the synthetic potential represented by the possibility of selectively activating one of two or more possible ketone targets by taking advantage of the distance between the donor and acceptor groups and/or their stereoelectronic relationship. In the study we describe below, we employ one aryl antenna group and two target ketone functionalities. The antenna, A, is a dimethylphenylsiloxy group (DPS), which we show to be an efficient singlet energy donor which can be readily attached to and detached from the molecule.[5] For the spacer which separates the aryl and ketone groups we utilize the rigid, chemically inert, steroidal androstane skeleton, which has been used by others to study intra-SSET[12,13] intra-

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