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A HIGHLY EFFICIENT RADICAL CLOCK AS A PROBE OF THE MECHANISM OF SULFONE HALOGENATION BY PERHALOALKANES

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Summary: Halogenation of (endo)-5-(2-i-propylsulfonyl)-2-norbornene 5, a new highly efficient radical probe, shows that if an SET mechanism was occurring in the α-halogenation of sulfones by perhaloalkanes, it would have to involve a reaction step in which a C-centered radical reacts with $CX_4^{\bar{\cdot}}$ at a rate greater than 10^{10} s^{-1} .

The reaction of sulfones with perhaloalkanes (CX_4) in basic media provides efficient access to α-halosulfonyl compounds[1]. Detailed mechanistic understanding remains elusive in these reactions

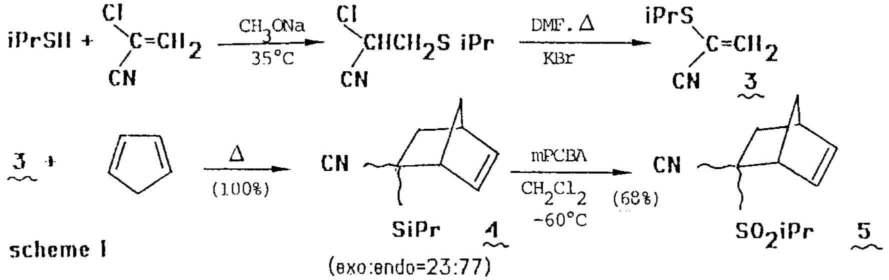
$$\underset{1}{R'SO_2CH_2R''} \xrightarrow[tBuOH]{KOH/CX_4} \underset{2}{R'SO_2CX_2R''}$$

both an S_N2-type mechanism with X-end attack[2] or monoelectron transfer from the carbanion to the perhaloalkane[1] have been proposed. In a recent article[3] we attempted to trap the proposed free radical intermediate 1b using (2-allyloxy)ethylphenylsulfone as the radical probe

$$\underset{1}{R'SO_2CH_2R''} \xrightarrow[tBuOH]{KOH} \underset{1a}{R'SO_2\ddot{C}HR''} \xrightarrow[e.t.]{CX_4} \underset{1b}{\left[R'SO_2\dot{C}HR''\,.CX_4^{\bar{\cdot}}\right]} \xrightarrow{-CX_3^{-}} R'SO_2CHXR''$$

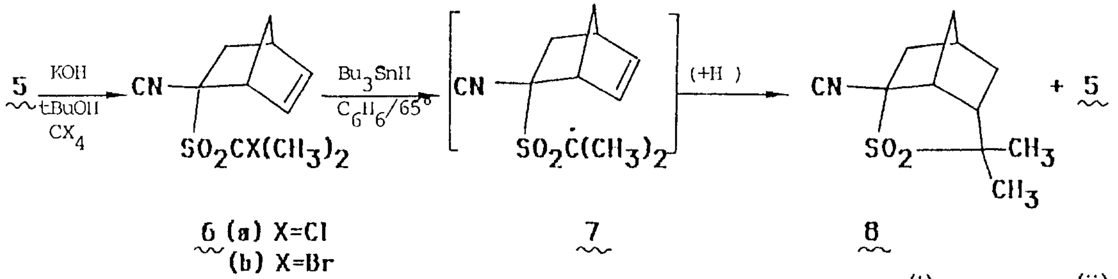
$R'=C_6H_5$,$R''=CH_2OCH_2CH=CH_2$. We concluded in that study that no radical intermediate with a life time $>10^{-6}$s was involved in the reaction path leading to halogenation. We describe here results obtained with an even faster radical probe. The present probe has a semi-rigid structure which favours intramolecular cyclization.

E.C.Ashby[4] recently described a new kind of free radical clock with a cyclization rate on the order of 10^7s^{-1}. With that report in mind we synthetized (endo)-5-cyano-5-(2-i-propylsulfonyl)-2 norbornene 5 from the Diels-Alder reaction[5] between cyclopentadiene and 1-cyano-1-i-propylthio ethylene[6] followed by oxydation of the sulfide to the sulfone. The dienophilic compound was obtained in two steps from i-propylthiol and 2-chloroacrylonitrile[7] (scheme 1). The pure



scheme I

(endo)-sulfone 5 is obtained by recrystallization from hexane-ether[8]. Halogenation of this compound leads, in practically quantitative yields, to the chloro (CCl_4,C_2Cl_6) or bromo (CBr_4, $CBrCl_3$) compounds (6a and 6b). In none of these halogenation reactions did we observe the cyclization product 8 (< 1% by HPLC and GPC)[9]. The cyclization product was unambigously prepared by reducing the chloro derivative 6a with tri-n-butyltin hydride using AIBN as initiator[10] (scheme II). Using a 6a/hydride ratio of 1:2.5, the cyclization product 8 is obtained in



Exp. 1$^{(i)}$. 8/5 = 100:0$^{(ii)}$
2 " = 93:7
3 " = 60:40

scheme II : Reaction of 6 with Bu_3SnH and AIBN(1% M) at 65°C in C_6H_6. (i) Experiments 1, 2, 3 refer respectively to nBu_3SnH / 6 ratios of: 2.5, 10 and 50. (ii) yields determined by HPLC analysis (Si 60, 7µm column, $CHCl_3$ as eluent).

quantitative yield. When increasing quantities of tri-n-butyltin hydride are employed, the yield of the reduction compound 5 increases, as expected. This increase in the yield of 5 (scheme II) allows an estimation of the cyclization rate for the radical 7 as being greater than $10^8 s^{-1}$.[11] To our knowledge, this is presently the fastest radical clock based on intramolecular cyclization.[12]

These experiments demonstrate that if an e.t. mechanism is involved in the reaction between α-sulfonyl carbanions and polyhaloalkanes, k_2 must be greater than approximatively $10^{10} s^{-1}$.

$$R'SO_2\bar{C}HR'' + CX_4 \xrightarrow{k_1} \left[R'SO_2\dot{C}HR''.\ CX_4^{\dot{-}}\right] \xrightarrow{k_2} R'SO_2CHXR'' + CX_3^{\dot{-}}$$

Thus, we must conclude that either S_H2 on X in radical anions are abnormally fast or that the displacement on X involving α-sulfonyl carbanion involves an S_N2-type transition state. We are presently performing theoretical calculations and spectroscopic experiments to more firmly establish this point.

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