## $\alpha$ - BENZENESULFONYL FREE RADICALS

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<u>Abstract</u> : Allylic  $\alpha$ -halosulfones give, on reduction with tri n-butyl tin hydride, sizeable amounts of dimers. It so appears that free radicals can indeed be formed  $\alpha$  to an arenesulfonyl group and coupling can occur during tin hydride reduction of halides.

Several recent results could be rationalised by way of  $\alpha$ -benzenesulfonyl free radicals <sup>(1-3)</sup>. Such free radicals are however not easily formed. In fact, free radical chlorination of alkylsulfones takes place not in the  $\alpha$ -position but the  $\beta$ -position and further <sup>(4)</sup>; so does the abstraction of hydrogen by hydroxyl radicals although phenyl radicals are more prone to  $\alpha$ -hydrogen abstraction <sup>(5)</sup>; phenylmethylsulfone is not dimerized by di t-butyl peroxide <sup>(6)</sup>. Next to hydrogen abstraction, the abstraction of halogen is a favourite way of generating free radicals. Tin hydrides have been extensively used by Kuivila <sup>(7)</sup> and others ; for instance in the generation of  $\beta$ -arenesulfonyl free radicals <sup>(8)</sup>. It is to be noted however that coupling of radicals has not been observed to be important under the conditions used <sup>(9)</sup>, transfer of hydrogen leading overwhelmingly to the overall exchange of halogen for hydrogen.

It has now been found that phenyl bromomethyl and phenyl  $\alpha$ -chlorododecyl <sup>(10)</sup> sulfones are quantitatively reduced to phenylmethyl resp. phenyldodecylsulfones when treated in boiling benzene with tri n-butyl tin hydride (1 éq.) and azo bis isobutyronitrile (1 eq.). In the absence of the free radical initiator the reaction is much slower.



When phenyl 1-chloro 3-methyl 2-butenylsulfone 2<sup>(11)</sup>, however, was similarly treated the 3-3' dimer 5 (30% yield) and some (5%) 1-3' dimer 6 were formed together with phenylprenylsulfone 4. We could detect no trace of the 1-1' dimer or phenyl 3-methyl 1-butenylsulfone 7<sup>(12)</sup>. A practically identical result was obtained with bromosulfone 3<sup>(13)</sup>. We checked that under the reaction conditions used no isomerisation of the  $\alpha$ -unsaturated sulfone 7 to the more stable  $\beta$ -isomer 4 took place. Equilibration of the E,Z mixture of 7 to the more stable E isomer took place instead, which is readily explained by addition elimination of tin radicals to the double bond.



The E/Z equilibration of vinylsulfones has been investigated (14).

This shows that the hydrogen transfer to the radical 1 in the  $\alpha$ -position is a kinetic process.

- \* The formation of free radicals to a sulfonyl group is probably made efficient by a polarity effect (5,15,16) since the tin radicals are electrondonating and  $\alpha$ -sulfonyl free radicals strongly electron accepting.
- \* The properties and uses of these free radicals will be investigated.
- \* The present results make it likely that free radicals are involved in the oxidative coupling of  $\alpha$ -sulfongl carbanions by copper (II) ions.

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