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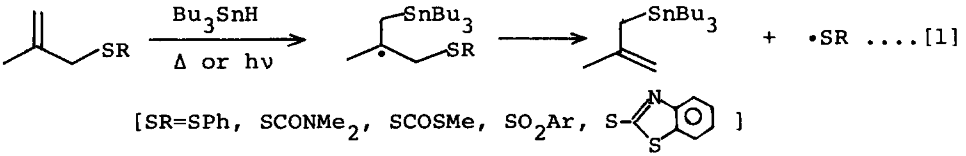
A NEW METHOD FOR THE EVALUATION OF THE RELATIVE STABILITY OF ORGANOSULFUR RADICALS BY COMPETITIVE ELIMINATION TECHNIQUE

Yoshio Ueno, Tadaaki Miyano, and Makoto Okawara
Research Laboratory of Resources Utilization , Tokyo Institute of Technology,
Nagatsuta, Midoriku, Yokohama 227, Japan

Summary: The relative stability of various organosulfur radicals is estimated by competitive elimination technique using tributyltin radical and acetophenone derivatives having two different sulfur substituents at α and α positions.

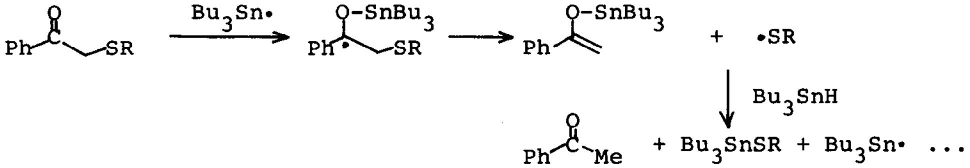
Organosulfur radicals have important roles in synthetic chemistry, polymer chemistry including rubber vulcanization, in air polution, and in the action of antioxidants and radioprotective agents.[1] Therefore, it is highly valuable to have an information on the relative stability of various organosulfur radicals. While, organotin hydride reductions have been broadly employed as useful mechanistic probes for homolytic reactions.[2] We have recently reported the new S_H' process involving organosulfur and tin radicals (eq. 1).[3]



....[1]

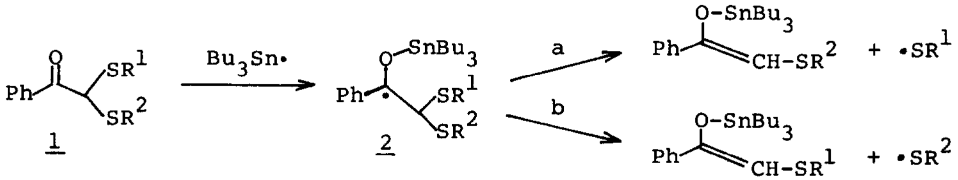
[SR=SPh, SCONMe$_2$, SCOSMe, SO$_2$Ar, S-]

In these reactions, no products were obtained derived from the direct attack of tin radical on sulfur atoms. It is highly anticipated that β-ketosulfides in place of allyl sulfides react similarly with tin radical to give desulfurized products.



...[2]

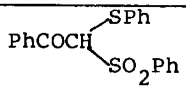
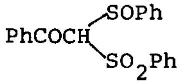
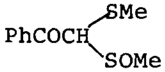
We found that this chain transfer reaction also proceeds cleanly under the similar conditions employed above.[4] Moreover, our interest has been directed to a system having two different sulfur substituents adjacent to carbonyl group as shown in eq. 3 (initial step).[4]



....[3]

The mode of cleavage from the initial adduct radical (2) [a *vs* b] should be highly depend on the stabilities of the eliminating radicals [R^1S• *vs* R^2S•]. To visualize our idea, we first examined the systems of thiyl, sulfinyl and sulfonyl radicals. Thus, the reduction of the suitable dithioacetals was carried out using an equimolar amount of tributyltin hydride in the presence of a catalytic amount of azobisisobutyronitrile (AIBN) at 80-100° for 1 h. The unexpectedly clean results were obtained; only one product was isolated in each case (Table 1). In each case, the product was isolated in high yield. For example, phenyl phenacyl sulfone was obtained in 99 and 88% yield in the cases of the compounds 3 and 4, respectively.[5,7]

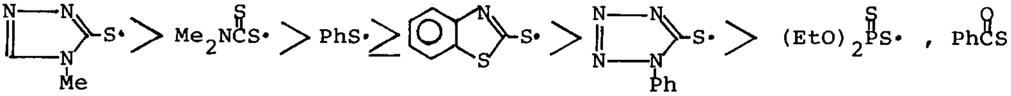
Table 1. Selective partial reduction of dithioacetals[8]

Substrate	Product	Eliminating radical
3  $PhCOCH(SPh)(SO_2Ph)$	$PhCOCH_2SO_2Ph$	PhS•
4  $PhCOCH(SOPh)(SO_2Ph)$	$PhCOCH_2SO_2Ph$	PhSO•
5  $PhCOCH(SMe)(SOMe)$	$PhCOCH_2SMe$	MeSO•

From the Table 1, differences in the stability of each pairs [PhS• > $PhSO_2$•, PhSO• > $PhSO_2$•, MeSO• > MeS•] lead to a conclusion that the relative stability among them increases in the order; PhSO• > PhS• > $PhSO_2$•. This result is consistent with the data obtained by the thermal dissociation study of S-S bonded compounds by Kice et.al., [ArSO• > ArS•, $ArSO_2$•].[9]

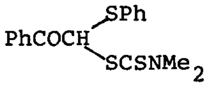
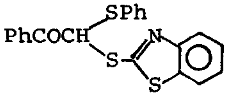
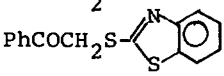
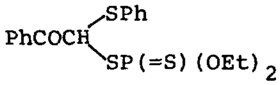
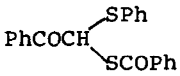
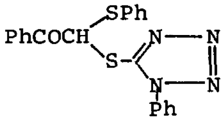
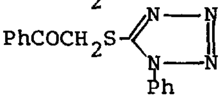
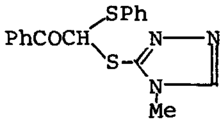
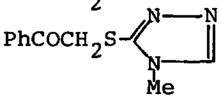
Next, the competitive elimination of the various sulfur radicals have been investigated. Some dithioacetals gave exclusively only one product, while, others afforded a mixture of desulfurized ketones (Table 2).

The results indicate the following stability order;



The present study demonstrates the quite noticeable differences in the splitting ability of various organosulfur groups. High stability of triazolylthio radical is a new information . It is presumably stabilized by the efficient delocalization of the unpaired electron through the ring system. On the other hand, tetrazolylthio radical is not so efficiently stabilized.

Table 2. Partial reductive desulfurization[8]

Substrate	Product	Ratio (%)[a]
6  $PhCOCH(SPh)SCSNMe_2$	$PhCOCH_2SPh$	86
	$PhCOCH_2SCSNMe_2$	14
7 	$PhCOCH_2SPh$	42
		58
8  $PhCOCH(SPh)SP(=S)(OEt)_2$	$PhCOCH_2SPh$	0
	$PhCOCH_2SP(=S)(OEt)_2$	100
9  $PhCOCH(SPh)SCOPh$	$PhCOCH_2SPh$	0
	$PhCOCH_2SCOPh$	100
10 	$PhCOCH_2SPh$	31
		69
11 	$PhCOCH_2SPh$	100
		0

[a] Estimated by ^{1}H-NMR spectroscopy.

These data are useful for the design of the chemicals or reactions involving organosulfur radicals as mentioned in the introduction. Furthermore, by the simple modification of the dithioacetal units, the method may predict the unknown stabilities of the wide variety of organosulfur radicals.

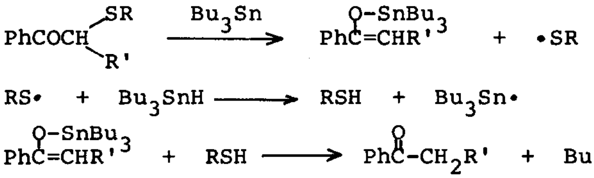
References and notes

1) E. Block, "Reactions of Organosulfur Compounds", Academic Press, New York, p 176-220 (1978).

2) M. Pereyre and J.-C. Pommier, "New Application of Organometallic Reagents in Organic Synthesis", D. Seyferth Ed., Elsvier, Amsterdam, p 161-183 (1976).

3) Y. Ueno, S. Aoki, M. Okawara, J. Am. Chem. Soc., 101, 5414 (1979);
Y. Ueno, H. Sano, M. Okawara, Tetrahedron Lett., 21, 1767 (1980);
Y. Ueno, M. Ohta, M. Okawara, J. Organometal. Chem., 197, C-1 (1980).

4) Final products were carbonyl compounds but not stannylenolethers. Unlike allylstannanes, stannylenolethers are more reactive and are easily converted to ketones by the attack of thiol.

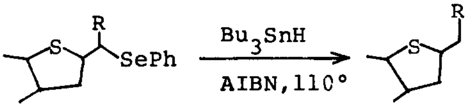


$$\mathrm{PhCOCH}\begin{smallmatrix}\mathrm{SR}\\ \mathrm{R'}\end{smallmatrix} \xrightarrow{\mathrm{Bu_3Sn}} \mathrm{Ph}\overset{\mathrm{O\text{-}SnBu_3}}{\mathrm{C}}\mathrm{{=}CHR'} + \bullet\mathrm{SR}$$

$$\mathrm{RS}\bullet + \mathrm{Bu_3SnH} \longrightarrow \mathrm{RSH} + \mathrm{Bu_3Sn}\bullet$$

$$\mathrm{Ph}\overset{\mathrm{O\text{-}SnBu_3}}{\mathrm{C}}\mathrm{{=}CHR'} + \mathrm{RSH} \longrightarrow \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{\text{-}CH_2R'} + \mathrm{Bu_3SnSR} \quad (\mathrm{R'{=}H,\ SR''})$$

5) Generally, sulfide, sulfoxide, sulfone or thiolester functions are inert towards organotin hydride as described in Ref. 3. While, selenides are practically reduced by tin hydride.



76%

K. C. Nicolaou, R. L. Mcgolda, W. J. Sipio, W. E. Barnetle, Z. Lysenko, M. M. Joullie, J. Am. Chem. Soc., 102, 3784 (1980);
Phenylsulfinylacetophenone was reduced with Bu_3SnH under UV irradiation to give acetophenone (>70%), while less reactive carbonyl species, phenylsulfinylacetone almost did not react with Bu_3SnH under similar conditions ($MeCOCH_2SOPh$ recovery >80%).

Furthermore, phenylsulfinylacetophenone gave thiostannane and sulfonylstannane in addition to acetophenone. (our unpublished data)

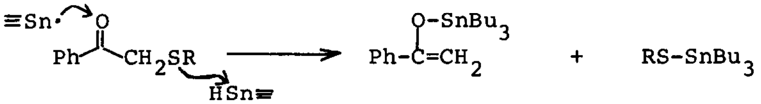
$$\mathrm{PhCOCH_2SOPh} + \mathrm{Bu_3SnH} \longrightarrow \mathrm{PhCOMe} + 1/2\ \mathrm{Bu_3SnSPh} + 1/2\ \mathrm{Bu_3SnSO_2Ph}$$

This result indicates the involvement of phenylsulfinyl radical and its well known disproportionation.[6]

All these facts show that the present reduction was initiated by the attack of tin radical to carbonyl oxygen atom but not to sulfur.

6) S. Oae, K. Ikura, Bull. Chem. Soc. Japan, 40, 1420 (1967).

7) Is there any participation of second tin hydride (or tin radical) molecule during the elimination as shown below?



$$\equiv\mathrm{Sn}\cdot\ \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{\text{-}CH_2SR}\ \ \mathrm{HSn}\equiv \longrightarrow \mathrm{Ph\text{-}}\overset{\mathrm{O\text{-}SnBu_3}}{\mathrm{C}}\mathrm{{=}CH_2} + \mathrm{RS\text{-}SnBu_3}$$

The high yield of reduced ketones (ca. 80-99%) under equimolar conditions excludes the above participation. Under the equimolar conditions, the yield should be less than 50% according to the above scheme.

8) In every runs, each product was isolated in reasonable to high yield and fully confirmed by the comparison with authentic samples.

9) J. L. Kice, N. E. Pawlouski, J. Am. Chem. Soc., 86, 4898 (1964).

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