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SYNTHESIS OF SULFENIC ACIDS: FLASH VACUUM PYROLYSIS OF ARYL AND ALKYL t-BUTYL SULFOXIDES

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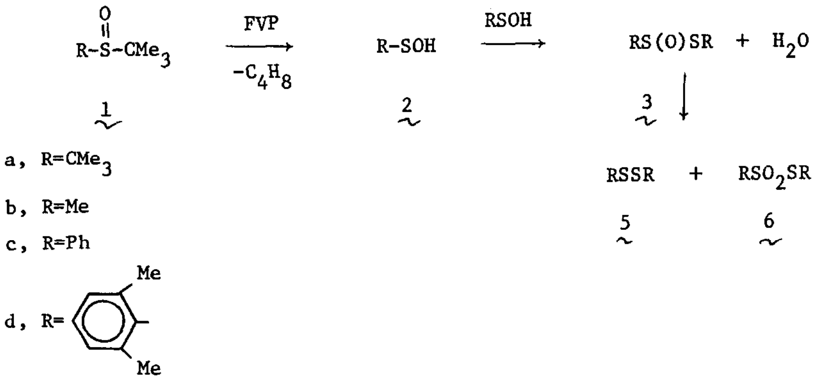
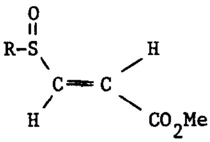
Sulfenic acids (RSOH) have been implicated as intermediates in a wide variety of important chemical transformations including biological reactions.[1] The high reactivity of these species and of their reaction products has hindered studies of their chemistry. Despite numerous attempts to prepare them, only a few very special examples are known.[2] The major reason for this is the lack of mild synthetic routes of these compounds.

The pyrolysis of aryl and alkyl sulfoxides containing a β-hydrogen atom is well known to afford the corresponding alkene and sulfenic acid via a concerted, stereospecific cis-elimination mechanism.[3] However, the temperatures required for this reaction to proceed at a convenient rate, ca 100-200°C, preclude studies of the labile sulfenic acids. Furthermore, the concentration of the sulfenic acid at any one time is very small.



We wish to report that flash vacuum pyrolysis (FVP)[4] of aryl and alkyl t-butyl sulfoxides is a convenient technique for preparing large concentrations of sulfenic acids under stable conditions. FVP of sulfoxides 1a-d[1b,5,6] with condensation of the pyrolyzate on a cold finger cooled to -196° affords the corresponding sulfenic acids, 2a-d in good to moderate yields. Evidence that the sulfenic acids are formed and stable under these conditions is revealed by the isolation of the corresponding labile thiolsulfinates (3) on thawing of the cold finger trap (Table).[7,8] The small amounts of disulfide, 5, and thiolsulfonate 6,[9] undoubtedly result from disproportionation of 3 on work-up.[10]

When t-butanesulfenic acid (2a) was co-condensed on the cold finger with a 5% methyl propiolate toluene solution a 69-73 per cent yield of adduct 4a was isolated by preparative TLC (silica gel) as an oil.[11] Briefly heating 4a in benzene with 1,3-diphenylisobenzofuran gave a 30 per cent yield of the Diels-Alder adduct 7.[12] Compound 4a has previously been proposed as a reactive intermediate in the formation of dimethyl trans, trans-sulfinyldiacrylate from



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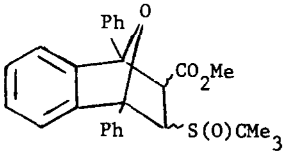

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1a and methy propiolate.[13] Stabilization of sulfenic acids by complexation with aromatic solvents has been proposed.[13] The higher yield of 4a obtained with a methyl propiolate-toluene solution compared with neat methyl propiolate is in accord with this proposal (Table : compare entries 3 and 4).

Sulfenic acids 2b-d failed to form adducts 4b-d under similar conditions. At higher temperatures and lower concentrations of the sulfenic acids, thermoylsis of 1b-d at 100° in a 5% methyl propiolate-toluene solution, adducts 4b-d were formed in excellent yield.[1b,13,14]

These results reveal that the most important reaction pathway for sulfenic acids when present in high concentration, i.e., FVP of 1a-d, is thiolsulfinate (3) formation. The unusual relative stability of t-butanesulfenic acid (2a) must be the result of steric inhibition of disproportionation (thiolsulfinate formation). Steric hinderance by the ortho methyl groups in 2d is apparently not sufficient to retard formation of 3d.

Methanesulfenic acid (2b) gave several unidentified products in addition to low yields of 3b, 5b, and 6b (Table, entry 6). Elemental sulfur and a polymeric residue were also detected. Block[1b] recently reported that the labile methyl methanethiolsulfinate (3b) can decompose to a variety of products. The sulfenic acid, 2b, may also be undergoing decomposition during pyrolysis. Elemental sulfur (ca 20%), water and a polymeric residue were the major products obtained when the FVP of 1b was carried out at 800°C. Elimination of water from 2b to form thioformaldehyde (CH_2=S) is in accord with these results although attempts to characterize the polymer have been unsuccessful. Block has recently detected thioformaldehyde in the microwave spectrum of 2b[15] .

Table: Flash Vacuum Pyrolysis of Aryl and Alkyl t-Butyl Sulfoxides at 1-2 x 10^{-2}torr.

entry	Sulfoxide	Pyrolysis Temperature C° (±10%)	Conditions[a]	Products[b] (% Yield)
1	1a	175	--	1a(64) 3a(2)
2		340	--	3a(93)
3		360	$HC{\equiv}CCO_2Me$	3a(10), 4a(40)
4		340	5%$HC{\equiv}CCO_2Me$ in toluene	4a(70), 3a(7)
5	1b	350	--	1b(70)
6		500[c]	--	3b(5), 5b(16), 6b(8)
7		500	5%$HC{\equiv}CCO_2Me$	3b(6), 5b(20), 6b(10)
8	1c	620	--	3c(58), 5c(6), 6c(10)
9		600	5%$HC{\equiv}CCO_2Me$ in toluene	3c(58), 5c(8), 6c(8)
10	1d	520	10%$HC{\equiv}CCO_2Me$ in toluene	3d(65), 5d(15), 6d(8)

a) Indicated reagent co-condensed with the pyrolyzate. Complete sulfoxide pyrolysis generally took 1-2 hrs. b) Isolated yields unless otherwise noted. Products were isolated by preparative TLC on silica gel. Reactions were performed at least twice and the results averaged. c) Products were identified by TLC and nmr. Yields were determined by nmr using an internal standard (triphenylmethane). Elemental sulfur and a polymeric residue were also isolated.

The FVP of aryl and alkyl t-butyl sulfoxides is a new and important source of stable sulfenic acids in high concentration. This technique will be of considerable value in studies of the reactions and properties of these elusive species. The isolation of good yields of aryl arenethiolsulfinates (3c-d) suggests that this method may also be a convenient source of these labile compounds.

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6. 2,6-Dimethylphenyl t-butyl sulfoxide (1d) isolated as an oil in 90% yield by oxidation of the corresponding sulfide (from the disulfide and t-butyllithium) with m-chloroperbenzoic acid had the following properties: ir (thin film) 1050cm^{-1} (s, S=O); nmr (CDCl$_3$)δ 1.3 (s, 9H, CMe$_3$), 2.1 (s, 3H, Me), 2.8 (s, 3H, Me) 7.0-7.3 (m 3H). A satisfactory elemental analysis was obtained.

7. Sulfenic acids are known to disproportionate according to the following equation: $2RSOH \longrightarrow RS(O)SR + H_2O$ see ref. 1,5 and E. Vinkler and F. Klivernyi, Int. J. Sulfur Chem. 8, 111 (1973).

8. 2,6-Dimethylphenyl 2,6-dimethylbenzenethiolsulfinate (3d) isolated by preparative TLC (silica gel) had the following properties: mp 89-91 (d); ir (KBr) 1100 cm.$^{-1}$ (s, S=O); nmr (CDCl$_3$) δ 2.15 (d, 12H, Me) and 7.2 (m, 6H). A satisfactory elemental analysis was obtained.

9. 2,6-Dimethylphenyl 2,6-dimethylbenzenethiolsulfonate (6d) isolated by preparative TLC (silica gel) had the following properties: mp 115-117°; ir (KBr) 1330 and 1160 cm^{-1} (s, SO$_2$); nmr (CDCl3) δ2.25 (s, 6H, Me), 2.5 (s, 6H, Me) and 7.0-7.4 (m, 6H). A satisfactory elemental analysis was obtained.

10. P.Koch, E. Ciuffarin and A. Fava, J. Am. Chem. Soc., 92 5971 (1970); D. Barnard, J. Chem. Soc., 4675 (1957).

11. Compound 4a had the following properties: ir (thin film) 1730 cm^{-1} (s, C=O), 1080 (s, S=O) nmr (CDCl$_3$) δ1.3 (s, 9H, CMe$_3$), 3.8 (s, 3H, OMe), AB quartet 6.3 (d, 1H, J=15Hz) and 7.7 (d, 1H, J=15Hz).

12. Compound 7 had the following properties: mp 139-41°; nmr (CDCl$_3$) δ 1.1 (s, 9H, CMe3), 3.2 (s, 3H, OMe), AB quartet 3.8 (d, 1H, J=4Hz) and 4.15 (d, 1H, J=4Hz) and 7.2-8.0 (m, 14H). A satisfactory elemental analysis was obtained.

13. J.R. Shelton and K.E. Davis, Int. J. Sulfur Chem., 8, 205 (1973).

14. Compound 4d was propared in 84% yield (isolation by preparative TLC on (silica gel) by heating 1d at 100°C with a 5% methyl propiolate toluene solution. Compound 4d had the following properties: mp 98-99; ir (KBr) 1720 (s, C=O) and 1080 cm^{-1} (m-s, S=O); nmr (CDCl$_3$) δ 2.55 (s, 6H, Me), 3.8 (s, 3H, MeO), AB quartet at 6.7 (d, 1H, J=15 Hz) and 7.7 (d, 1H, J=15Hz) and 7.1 (m, 3H). A satisfactory elemental analysis was obtained.

15. Personal communication from E. Block.