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THE REACTION OF MERCAPTANS WITH DIMETHYLDIOXIRANE. A FACILE SYNTHESIS OF ALKANESULFINIC ACIDS.

D. GU AND DAVID N. HARPP*

Department of Chemistry
801 Sherbrooke St. W.
McGill University
Montreal, Quebec, Canada H3A 2K6

Summary: Dimethyldioxirae oxidizes aliphatic thiols to sulfinic acids in very good yield. Benzylic and aromatic thiols give a variety of other oxidation products using DMD.

Several methods are available for the synthesis of sulfinic acids.[1] Most of them are carried out through indirect and multi-step routes. The "interval oxidation" of alkanethiols (C2-C4) by *m*-chloroperbenzoic acid (MCPBA) yields sulfinic acids in good yield and purity.[2] However, this method involves a troublesome operation of filtration at low temperature.

Here, we report a new procedure for the one step preparation of alkanesulfinic acids. This method involves the oxidation of alkanethiols by dimethyldioxirane (DMD), a powerful electrophilic oxidant.[3] The oxidation reaction is carried out at -40°C. Our preliminary experiments indicated that it was difficult to prevent the formation of sulfonic acid if two equivalents of DMD were used, and the "interval" addition of DMD made no improvement.

It was found that slow addition of 1.2 equivalents of DMD to 1 equivalent of thiol in dichloromethane under a nitrogen atmosphere, followed by exposure of the reaction solution to the air, provides alkanesulfinic acids (C2-C5) in very good yield and high purity. The experimental results are summarized in Table 1.

Table 1. Experimental Results for the DMD/Alkanethiol Reactions.

Reagent	Yield(%)	Product
CH_3CH_2SH	73	$CH_3CH_2SO_2H$[a]
$CH_3CH_2CH_2SH$	74	$CH_3CH_2CH_2SO_2H$[b]
$(CH_3)_2CHSH$	90	$(CH_3)_2CHSO_2H$[c]
$CH_3CH_2CH_2CH_2SH$	84	$CH_3CH_2CH_2CH_2SO_2H$[d]
$(CH_3)_3SH$	95	$(CH_3)_3SO_2H$[d]
$CH_3(CH_2)_4SH$	96	$CH_3(CH_2)_4SO_2H$[d]

[a]The purity was checked by ^1H NMR at *ca.* 100%; the relatively low yield may come from the high volatility of this acid being lost in the solvent-removal procedure; [b]93% purity by ^1HNMR; the side product was the sulfonic acid; [c]97% purity by ^1H NMR; the side product was the sulfonic acid; [d]The product contained a trace of solvent; no sulfonic acid was observed by ^1H NMR.

A reasonable mechanism for this oxidation reaction would likely involve the thiol being oxidized to the sulfenic acid by DMD followed by sulfenic acid oxidation to sulfinic acid by either DMD or air oxidation. (Scheme 1).

Scheme 1

Under the same reaction conditions, *i.e.*, -40°C and 1.2 equivalents of DMD, benzyl mercaptan and *p*-thiocresol gave several products with sulfinic acid as the major one. Tables 2 and 3 summarize the experimental results.

Table 2. Product Distribution of DMD/Benzyl Mercaptan Oxidation.

Compound[a]	$BzSO_2H$[b]	$BzSO_3H$	BzSH	BzSSBz	$BzSO_2SBz$	C_6H_5CHO
Rel. Amt.(%)[c]	71	5	8	7	7	2

[a]The compounds were identified by ^{13}CNMR. The chemical shifts of the benzyl carbon agree with the literature;[4] [b]Bz = $C_6H_5CH_2$; [c]The relative amounts for thiosulfonate, disulfide, mercaptan and benzaldehyde were determined by gas chromatography. The amounts of sulfinic and sulfonic acid were estimated by ^{13}C NMR. ^1H NMR was used to obtain the total ratio of acids to the other compounds.

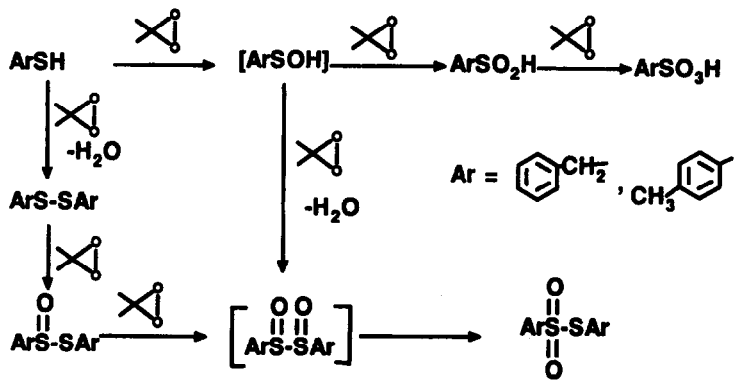
Table 3. Product Distribution of DMD/*p*-Thiocresol Oxidation.

Compound[a]	$ArSO_2H$[b]	$ArSO_3H$	ArSSAr	$ArSO_2SAr$
Rel. Amt.(%)[c]	18	29	33	20

[a]All of these compounds were identified by ^1H NMR using acetone-d_6 as solvent and TMS as standard. The chemical shifts of the methyl proton of these compounds are the same as the authentic samples (δ, $-SO_2H$, 2.40; $-SO_3H$, 2.43; -SS-, 2.30; $-SO_2S-$, 2.37, 2,43. GLC analysis also indicates the presence of the disulfide and thiosulfonate; [b]Ar = p-$CH_3C_6H_4$; [c]Other minor components are not listed; [d] The relative amounts were derived from the integral of the 1H NMR experiment.

A possible mechanism for the DMD oxidation of benzyl mercaptan and p-thiocresol is portrayed in Scheme 2.

Scheme 2

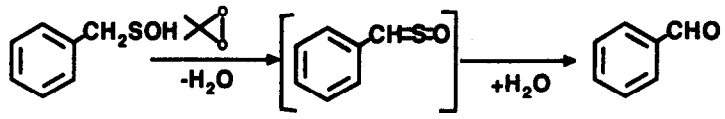


In the DMD/*p*-thiocresol reaction and the DMD/benzyl mercaptan reaction, sulfinic and sulfonic acids, disulfides and thiosulfonates were formed. In these cases, oxidation/dehydration among two equivalents of thiol and one equivalent of DMD yielded disulfide. The presence of sulfonic acids is likely due to the further oxidation of sulfinic acids.

There are two possible pathways leading to the formation of thiosulfonate. One is that the disulfide is oxidized to thiosulfinate which is further oxidized to the α-disulfoxide.[5] It is well-known that the rearrangement of α-disulfoxides lead to the formation of thiosulfonates.[5a,b] Another pathway is that the dehydration between two equivalents of sulfenic acid and one of DMD gives the α-disulfoxide. The experimental result seems to favor the second pathway since little thiosulfinate is observed in the oxidation products. However, the first pathway can not be ruled out because the thiosulfinate is not a stable compound.

Trace amounts of benzaldehyde resulted in the DMD/benzyl mercaptan reaction. It is likely that dehydration between one equivalent of benzyl sulfenic acid and one equivalent of DMD would give an intermediate sulfine; the hydration of the sulfine would lead to aldehyde (Scheme 3). It was also discovered that benzaldehyde was a major side product when this reaction was carried out at room temperature.

Scheme 3



A typical procedure for the alkyl thiols follows. Alkanethiol (1 mmol) in dry dichloromethane (10 mL) was stirred at -40°C (dry ice/isopropanol bath) under N_2. DMD (1.2 mmol) was added dropwise for one hour through a pressure-equalized dropping funnel equipped with a dry ice-cooling jacket to cool the DMD. After the addition of DMD, the solvent was removed by blowing N_2 at the surface of the solution. The solution was kept in an evacuated desiccator (P_2O_5) for a short period (15 min) to remove the moisture. The total operation takes less than 2 h. Corroborative spectral data are listed in Table 4.

Table 4. Spectral Data for Alkanesulfinic Acids.

Acid	^{1}H NMR	^{13}C NMR[4a]
ethanesulfinic	1.27(t,3H), 2.81(q, 2H) J = 7.6Hz	5.48, 51.12
1-propanesulfinic	1.06(t,3H), 1.75(m,2H), 2.79(t,2H) JH_1-H_2 = 7.6Hz, JH_2-H_3 = 7.4Hz	13.25, 15.31, 59.40
2-propanesulfinic	1.25(d,6H), 2.77(m,1H), J = 6.9Hz	13.81, 55.21
1-butanesulfinic	0.96(t,3H), 1.46(m,2H), 1.68(m,2H), 2.81(t,2H) JH_1-H_2 = 7.4Hz, JH_3-H_4 = 7.1Hz	13.72, 21.86, 23.55, 57.41
2-methyl-2-propanesulfinic	1.20(s,9H)	21.32, 56.56
1-pentanesulfinic	0.91(t,3H), 1.34(m,4H), 1.88(m,2H), 2.79(t,2H) JH_1-H_2 = 7.7Hz, JH_4-H_5 = 7.2Hz	13.79, 22.30, 21.24, 30.75, 57.61

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