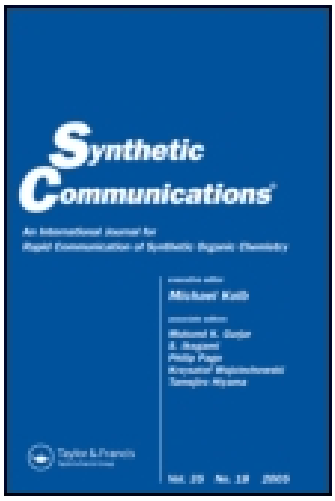

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A SELECTIVE AND CONVENIENT OXIDATION OF ACETYLENIC SULFIDES TO ACETYLENIC SULFOXIDES USING TRICHLOROISOCYANURIC ACID

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ABSTRACT

Acetylenic sulfides are readily oxidized to acetylenic sulfoxides by a solution of pyridine, water, benzoic acid and trichloroisocyanuric acid in acetonitrile and methylene chloride.

Acetylenic sulfoxides are useful building blocks in organic synthesis.[1] The selective oxidation of sulfides to sulfoxides is an attractive and extremely important method. Acetylenic sulfides can be converted into acetylenic sulfoxides using various oxidizing agents.[1–5] Trichloroisocyanuric acid [1,3,5-trichloro-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione] has been a useful reagent in organic synthesis,[6] it has been used to oxidized secondary alcohol to ketones in good yields.[7] We have now found that trichloroisocyanuric acid [1,3,5-trichloro-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione] (**2**) is very efficient, highly selective reagent for oxidation of acetylenic sulfides into acetylenic sulfoxides.

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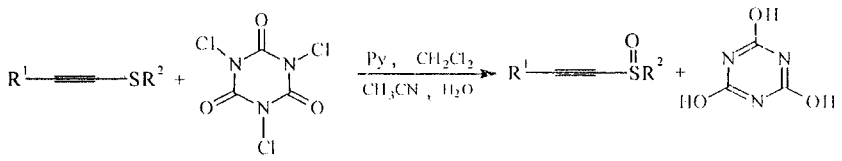
A solution of acetylenic sulfide **1**, pyridine, water, benzoic acid and **2** in acetonitrile and methylene chloride underwent oxidation to produce the corresponding acetylenic sulfoxide **3** along with cyanuric acid **4** and hydrogen chloride. Yields are good to excellent (Scheme 1 and Table 1).



1 **2** **3** **4**

R^1 = Ph, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, CH_3OCH_2;

R^2 = Ph, 4-MeC_6H_4

Scheme 1.

Although acetonitrile generally worked well, in some instances other solvents such as methelene chloride were more suitable due to that some acetylenic sulfides have relative poor solubility in acetonitrile. To enhance the rate of oxidation a trace of water was added to the acetylenic sulfide reaction mixture. In absolute anhydrous condition the reaction hardly proceed under similar conditions. But excessive water will reduce the rate

Table 1. Synthesis of Compounds **3a–i**

Product	R^1	R^2	Yield (%)[a]
3a	Ph	Ph	86
3b	*n*-C_4H_9	Ph	89
3b[b]	*n*-C_4H_9	Ph	58
3c	*n*-C_5H_{11}	Ph	90
3d	Ph	4-MeC_6H_4	91
3e	*n*-C_3H_7	4-MeC_6H_4	88
3f	*n*-C_4H_9	4-MeC_6H_4	94
3g	*n*-C_5H_{11}	4-MeC_6H_4	93
3h	*n*-C_6H_{13}	4-MeC_6H_4	90
3i	CH_3OCH_2	4-MeC_6H_4	82

[a]Isolated yield.
[b]Without benzoic acid.

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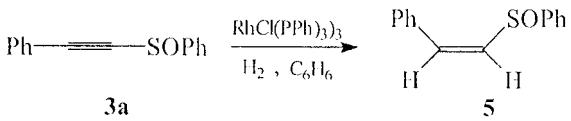
of oxidation and give poor yields. Since hydrogen chloride is produced in the reaction and it can then react with **2** to form chlorine,[8] pyridine is used to react with hydrogen chloride to form pyridine hydrochloride. Without benzoic acid in the reaction mixture the products **3** were produced in only 50–60% yields along with a few byproducts.

Although the ease of the reactions is dependent on the electrosteric properties of the acetylenic sulfides, it should be emphasized that the reactions could been performed cleanly and controlled to stop at the sulfoxides stage. There was no evidence for the formation of any sulfones, which enabled easy isolation of the sulfoxides.

Acetylenic sulfoxides **3** have recently emerged as valuable reagents for organic synthesis. For example, acetylenic sulfoxide **3a** was transformed into (*Z*)-((2-phenylethenyl)sulfinyl)benzene **5** in 93% yield by treatment with $[RhCl(PPh_3)_3]$ under hydrogen. (Scheme 2)



3a **5**

Scheme 2.

EXPERIMENTAL

^{1}H NMR spectra were recorded on AZ-300 spectrometer with TMS as internal standard. IR spectra were determined on PE-683 instrument as neat films. Silica gel 60 GF254 was used for analytical and preparative TLC. All products were characterized by comparison with authentic samples using IR, ^{1}H NMR and GC retention time. The acetylenic sulfides were prepared from aryl sulfenyl chlorides and acetylenic lithium.[3]

General Procedure for the Synthesis of 3a–i: In a 25 ml two-neck flask were placed 2 mmol of acetylenic sulfide **1**, 2 mmol of benzoic acid, 2 ml of acetonitrile, 2 ml of methylene chloride, 0.1 ml of water. The mixture in flask was allowed to stir for 5 min before the addition of the solution of **2** was started. The solution of **2** (1.5 mmol) in 1 ml of acetonitrile was added dropwise through a syringe. After a few minutes, the reaction temperature began to rise. The addition took a total of 15 min and that was followed by an additional 30 min of stirring at 40°C. Excess **2** was destroyed by the slow addition of saturated $NaHSO_3$ solution. During this process, wet iodide-starch test paper was used to periodically test for the presence of oxidizing power. The precipitate of cyanuric acid **4** was removed by

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filtration and washed with diethyl ether. Most of the solvent was removed from the filtrate with a rotary evaporator and the residue was diluted with 20 ml of diethyl ether. The ether solution was washed with 1 N NaOH (2×3 ml), 1 N HCl (2×3 ml), and saturated NaCl solution (2×3 ml) and dried over $MgSO_4$. After filtration and concentration, the crude product was purified by preparative TLC on silica gel and eluted with hexane and ethyl acetate (5/1).

3a: oil. ^{1}H NMR: $\delta = 7.70$–7.20 (m, 10H); IR (film) $\nu = 3082$, 2175, 1525, 1480, 1455, 1045, 1020 cm^{-1}. Calc. for $C_{11}H_{10}OS$: C, 74.31; H, 4.45. Found: C, 74.45; H, 4.43%.

3b: oil. ^{1}H NMR: $\delta = 7.57$–7.92 (m, 5H, C_6H_5), 2.33 (m, 2H), 0.63–1.53 (m, 7H); IR (film) $\nu = 3070$, 3030, 2950, 2180, 1550, 1450, 1088, 1055, 1030 cm^{-1}. Calc. for $C_{12}H_{14}OS$: C, 69.86; H, 6.84. Found: C, 69.45; H, 6.78%.

3c: oil. ^{1}H NMR: $\delta = 7.60$–710 (m, 5H, C_6H_5), 2.28 (m, 2H), 0.65–1.50 (m, 9H); IR (film) $\nu = 2980$, 2185, 1600, 1500, 1085, 1045, 1015 cm^{-1}. Calc. for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.49; H, 7.43%.

3d[9]**:** a yellow solid, mp: 78–79°C (lit.[9]: 78–79°C). ^{1}H NMR: $\delta =$ 7.70–7.00 (m, 9H), 2.30 (s, 3H); IR (film) $\nu = 3080$, 2940, 2900, 2150, 1495, 1450, 1055, 1020 cm^{-1}. Calc. for $C_{15}H_{12}OS$: C, 74.97; H, 5.03. Found: C, 75.12; H, 5.01%.

3c[10]**:** oil. ^{1}H NMR: $\delta = 7.60$ (d, $J = 8$ Hz, 2H, C_6H_4), 7.25 7.22 (d, $J = 8$ Hz, 2H, C_6H_4), 2.43 (s, 3H, $CH_3C_6H_4$) 2.38 (t, $J = 7$ Hz, 2H), 1.60–1.00 (m, 5H); IR (film) $\nu = 2900$, 2190, 1600, 1495, 1090, 1055, 1020 cm^{-1}. Calc. for $C_{12}H_{14}OS$: C, 69.86; H, 6.84. Found: C, 69.45; H, 6.78%

3f[10]**:** oil. ^{1}H NMR: $\delta = 7.58$ (d, $J = 8$ Hz, 2H, C_6H_4), 7.22 (d, $J = 8$ Hz, 2H, C_6H_4), 2.42 (s, 3H, $CH_3C_6H_4$) 2.36 (t, $J = 6$ Hz, 2H), 1.85–0.85 (m, 7H); IR (film) $\nu = 2900$, 2190, 1600, 1495, 1090, 1055, 1020 cm^{-1}. Calc. for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.59; H, 7.43%.

3g[10]**:** oil. ^{1}H NMR: $\delta = 7.60$ (d, $J = 8$ Hz, 2H, C_6H_4), 7.24 (d, $J = 8$ Hz, 2H, C_6H_4), 2.42 (s, 3H, $CH_3C_6H_4$) 2.36 (t, $J = 6$ Hz, 2H), 1.85–0.90 (m, 9H); IR (film) $\nu = 2980$, 2190, 1600, 1495, 1090, 1055, 1020 cm^{-1}. Calc. for $C_{14}H_{18}OS$: C, 71.75; H, 7.74. Found: C, 71.66; H, 7.63%.

3h[10]**:** oil. ^{1}H NMR: $\delta = 7.68$ (d, $J = 8$ Hz, 2H, C_6H_4), 7.32 (d, $J = 8$ Hz, 2H, C_6H_4), 2.44 (s, 3H, $CH_3C_6H_4$) 2.36 (t, $J = 6$ Hz, 2H), 1.80–0.90 (m, 11H): IR (film) $\nu = 2980$, 2190, 1600, 1495, 1090, 1055, 1020 cm^{-1}. Calc. for $C_{15}H_{20}OS$: C, 72.53; H, 8.11. Found: C, 72.72; H, 8.03%.

3i[1]**:** oil. ^{1}H NMR: $\delta = 7.65$ (d, $J = 8$ Hz, 2H, C_6H_4), 7.25 (d, $J = 8$ Hz, 2H, C_6H_4), 4.25 (s, 3H, CH_2O), 3.35 (s, 2H, CH_3O), 2.43 (s, 3H, $CH_3C_6H_4$); IR (film) $\nu = 2940$, 2825, 2180, 1595, 1105, 1060, 1015 cm^{-1}. Calc. for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.59; H, 5.87%.

The Synthesis of (*Z*)-((2-Phenylethenyl)sulfinyl)benzene 5: A solution of **3a** (1 mmol) in anhydrous benzene (15 ml), degassed twice by lyophilization

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and replacement with nitrogen, was added to $RhCl(PPh_3)_3$, (0.03 mmol) under hydrogen. The mixture was hydrogenated overnight (24 h) at room temperature under an atmospheric pressure. The mixture was diluted with ether and passed through a short column of silica gel. Removal of the solvent under reduced pressure followed by chromatography of the residure on silica gel (hexane/EtOAc, 5:1), gave the (*Z*)-((2-phenylethenyl)sulfinyl)-benzene **5** in 93% yield.

5[11]: oil. ^{1}H NMR: $\delta = 7.70$–7.20 (m, 10H, Ph), 7.05 (d, $J = 10.5$ Hz, 1H), 6.40 (d, $J = 10.5$ Hz, 1H); IR (film) $\nu = 3085$, 3010, 1605, 1500, 1040 cm^{-1}. Calc. for $C_{14}H_{12}OS$: C, 73.65; H, 5.30. Found: C, 73.59; H, 5.41%.

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