BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (10), 3081—3082 (1978)

Reaction of α-Keto Sulfoxides with Hydrogen Chloride and Trichloroacetic Acid

Toshimitsu Wakui, Yoshio Nakamura, and Shinichi Motoki*

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

(Received December 22, 1977)

Synopsis. α-Keto sulfoxides (**1**) reacted with hydrogen chloride to afford chloroformates, disulfides, and thiosulfonates. **1** also reacted with trichloroacetic acid to give methyl trichloroacetate, disulfide and thiosulfonate.

α-Keto sulfoxides have been postulated as unstable intermediates in the thiocarboxylic *S*-acid oxidation with NBS, iodosobenzene,[1] and *m*-chloroperbenzoic acid[2] and isolated as stable compounds by oxidizing thiocarbonate *O*,*S*-diesters and related substances with *m*-chloroperbenzoic acid.[3] This new class of organic compounds are interesting and have attracted the attention of organic chemists to their chemical behavior.

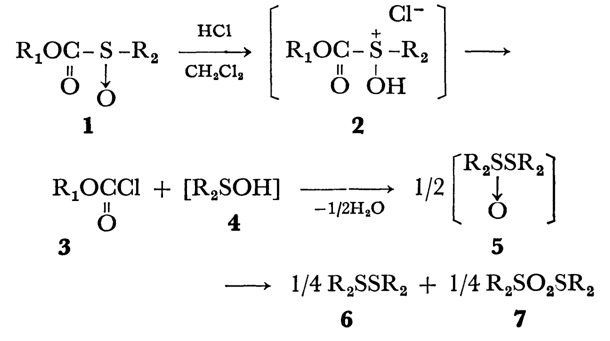
Recent studies by Chaves das Neves and Machete have shown that ethoxycarbonyl benzyl sulfoxide reacts with thionyl chloride and *S*-benzyl *O*-ethyl thiocarbonate.[4] Furukawa and his co-workers also reported that benzyloxycarbonyl benzyl sulfoxide reacts with acetic anhydride to give 1-(acetylthio)benzyl sulfoxide together with other products.[5] In this note, the reactions of α-keto sulfoxides with hydrogen chloride and trichloroacetic acid will be reported.

Dry hydrogen chloride was bubbled at room temperature for 2 h into a solution of phenoxycarbonyl ethyl sulfoxide (**1a**) in dichloromethane. After the solution was stirred for an additional 20 h, it was shown by TLC that **1a** was consumed, and from the reaction mixture, phenyl chloroformate (**3a**), diethyl disulfide (**6a**) and *S*-ethyl ethanethiosulfonate (**7a**) were isolated in fairly good yields. The structures of the products were determined from their spectroscopic data.

In the reactions of methoxycarbonyl benzyl sulfoxide (**1b**), methoxycarbonyl phenyl sulfoxide (**1c**) and ethoxycarbonyl benzyl sulfoxide (**1d**) with hydrogen chloride, the yields of alkyl chloroformates (**3**) were determined by conversion into the alkyl phenyl carbonate derivatives. The disulfides (**6**) and the thiosulfonates (**7**) were separated by column chromatography using benzene–petroleum ether (1 : 1) as the eluent. The reaction of benzyloxycarbonyl benzyl sulfoxide (**1e**) with hydrogen chloride similarly gave benzyl chloroformate (**3e**), dibenzyl disulfide (**6e**) and *S*-benzyl toluene-α-thiosulfonate (**7e**). The yields of **3e** and **6e** were calculated by the integrated ratio of the PMR spectrum of the mixture since they could not be separated by ordinary column chromatography. The results are shown in Table 1.

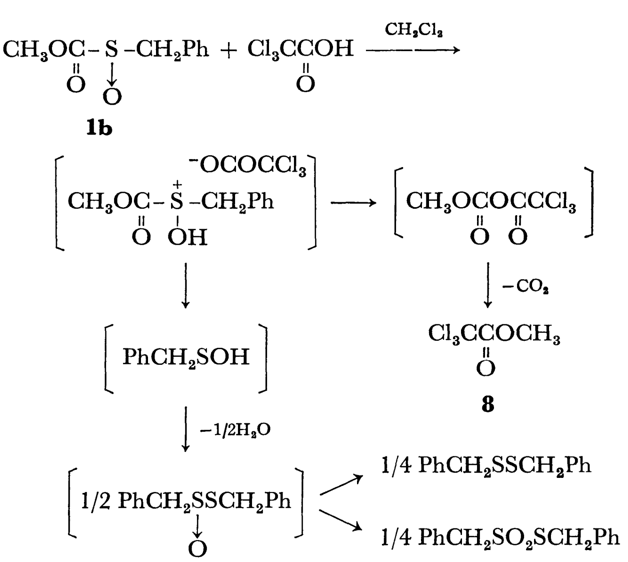
Table 1. Reaction of α-keto sulfoxides **1** with hydrogen chloride

α-Keto sulfoxide	R_1	R_2	Yield (%)		
			3	**6**	**7**
1a	Ph	Et	74	63	76
1b	Me	$PhCH_2$	69	90	91
1c	Me	Ph	59	99	84
1d	Et	$PhCH_2$	57	92	93
1e	$PhCH_2$	$PhCH_2$	65	86	93



Scheme 1.

The reaction probably proceeds *via* an initial protonation of the sulfoxide **1** affording an unstable sulfonium ion such as **2** which is further converted to the alkyl (or aryl) chloroformate **3** and the sulfenic acid **4**. Then **4** may give the thiosulfinate **5** which disproportionates further to give the final products, the disulfide **6** and the thiosulfonate **7**. This scheme is based on the observation that the sulfenic acids afford water and the thiosulfinates through dimerization[6] while the thiosulfinates smoothly disproportionate in acidic conditions to the disulfides and the thiosulfonates.[7]



Scheme 2.

Both the reaction of **1d** with hydrogen chloride and with thionyl chloride gave closely similar products such as ethyl chloroformate, dibenzyl disulfide, and *S*-benzyl toluene-α-thiosulfonate, but the yields of the products are better in the former case.

When a solution of **1b** and trichloroacetic acid in dichloromethane was refluxed for 15 h, methyl trichloroacetate (**8**, 42%), dibenzoyl disulfide (40%) and *S*-benzyl toluene-α-thiosulfonate (46%) were the products. These results may be rationalized according to Scheme 2.

Experimental

All the melting and boiling points are uncorrected. The IR spectra were obtained on a 260-10 Hitachi Model infrared spectrophotometer. PMR spectra were recorded with a JEOL JNM-PMX 60 spectrometer, in $CDCl_3$ solution with TMS as an internal standard.

Materials. α-Keto sulfoxides **1d** and **1e** were obtained by the methods described in the literature.[3] Other α-keto sulfoxides **1a**—**c** were prepared in a similar manner and their physical properties are as follows: **1a**: mp 67—69 °C; IR (Nujol): 1760 cm^{-1} (C=O); PMR (δ): 1.27 (t, 3H), 2.85 (q, 2H), 7.17 (s, 5H). **1b**: mp 81 °C; IR (Nujol): 1765 cm^{-1} (C=O); PMR (δ): 3.92 (s, 3H), 4.23 (s, 2H), 7.33 (s, 5H). **1c**: mp 77—78 °C; IR (Nujol): 1760 cm^{-1} (C=O); PMR (δ): 3.93 (s, 3H), 7.70 (m, 5H).

*General Procedure for Reactions of α-Keto Sulfoxides (**1**) with Hydrogen Chloride.* Dry hydrogen chloride was bubbled at room temperature for 2 h with stirring into a solution of **1** (3–23 mmol) in dichloromethane. The reaction mixture was stirred at the same temperature for 20 h and each product was separated as follows.

1a: After the solvent had been removed under reduced pressure, distillation of the residue gave 0.44 g (63%) of diethyl disulfide (**6a**), bp 50—60 °C/31 Torr, 2.68 g (74%) of phenyl chloroformate (**3a**), bp 60—62 °C/8 Torr, and 0.68 g (76%) of *S*-ethyl ethanethiosulfonate (**7a**), bp 90—100 °C/5 Torr.

1b: The solvent and methyl chloroformate (**3b**) were distilled under reduced pressure. The distillate was then added to a solution of phenol (0.94 g, 10 mmol) and triethylamine (5 g, excess) in ether (50 ml) and the mixture stirred for 5 h. Water (100 ml) was added to the mixture and the organic layer that separated, was successively washed with dilute sodium hydroxide solution, dilute hydrochloric acid, and water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to afford 0.95 g (69%) of methyl phenyl carbonate.

The residue obtained after the solvent and **3b** had been removed, was column chromatographed on silica gel C-200. Elution with benzene–petroleum ether (1: 1) gave 0.50 g (90 %) of dibenzyl disulfide (**6b**), mp 68.5—69 °C, and 0.57 g (91 %) of *S*-benzyl toluene-α-thiosulfonate (**7b**), mp 108—109 °C.

1c, 1d: The products obtained by the reactions of **1c** and **1d** with hydrogen chloride were isolated in a similar manner as above.

1e: After the solvent had been removed under reduced pressure, the residue was subjected to column chromatography on silica gel to afford the mixture of benzyl chloroformate (**3e**) and dibenzyl disulfide (**6e**), and 0.20 g (96%) of *S*-benzyl toluene-α-thiosulfonate (**7e**) by elution with benzene–petroleum ether (1: 1). The yields of **3e** and **6e** (as determined by PMR) were 65 and 86%, respectively.

*Reaction of **1b** with Trichloacetic Acid.* A mixture of **1b** (1.78 g, 9 mmol) and trichloroacetic acid (1.47 g, 9 mmol) in dichloromethane (30 ml) was refluxed for 15 h and the solvent removed under reduced pressure. The residue was distilled to give 0.63 g (42%) of methyl trichloroacetate (**8**), bp 50—56 °C/19 Torr. The residue obtained after distillation was dissolved in ether (100 ml) and the solution succesively washed with water, dilute sodium hydroxide solution, and water. After being dried over anhydrous sodium sulfate, the solvent was removed. The residue was column chromatographed on silica gel to afford 0.22 g (40%) of dibenzyl disulfide and 0.29 g (46%) of *S*-benzyl toluene-α-thiosulfonate, by elution with benzene–petroleum ether (1:1).

References

1) T. Kumamoto and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **41**, 2111 (1968).

2) H. Minato, H. Kodama, T. Miura, and M. Kobayashi, *Chem. Lett.*, **1977**, 413.

3) D. H. R. Barton, D. P. Manly, and D. A. Widdowson, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1568.

4) H. J. Chaves das Waves and M. F. Machete, *Tetrahedron Lett.*, **1977**, 187.

5) N. Furukawa, T. Morishita, T. Akasaka, and S. Oae, *Tetrahedron Lett.*, **1977**, 1653.

6) J. R. Shelton and K. E. Davis, *J. Am. Chem. Soc.*, **89**, 714 (1967).

7) E. Brock and S. W. Weidman, *J. Am. Chem. Soc.*, **95**, 5046 (1973); D. Barnard, *J. Chem. Soc.*, **1957**, 4675; S. Oae and S. Kawamura, *Bull. Chem. Soc. Jpn.*, **35**, 1156 (1962).