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### Chromium trioxide-acetic acid as a spray for organosulfur compounds

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Since the report by Loeppky and Chang<sup>1</sup> in 1968 of a method for the chlorination of sulfoxides, a growing interest in the development of new methods for the preparation of  $\alpha$ -chlorinated sulfoxides has become evident<sup>2</sup>.

Very recently, a thin-layer chromatography (TLC) spray, ammonium hexanitratocerate(IV) solution, was reported by Grossert and Langler<sup>2</sup> to permit the detection of  $\alpha$ -polychlorosulfoxides containing up to four  $\alpha$ -chlorine atoms. This spray showed a sharp decline in sensitivity with increasing chlorine content in the sulfoxides.

Chromium trioxide in acetic acid (Fieser's reagent) has been known as a potent oxidizing agent for some time<sup>3,4</sup>. Indeed, it has been utilized by Truce *et al.*<sup>5</sup> to oxidize a number of the sulfides reported here to the corresponding sulfones. Furthermore, Grossert and Langler<sup>6</sup> have successfully oxidized all of the  $\alpha$ -chlorinated sulfoxides reported here to the corresponding sulfones following the procedure of Truce *et al.* In solution, the deep purple color of  $\text{CrO}_3$  is changed to deep green as the reaction proceeds and the concentration of  $\text{Cr}^{3+}$  ions increases.

#### EXPERIMENTAL

The origin of compounds 1-3 and 6-26 has been detailed in the previous article<sup>2</sup>. Compound 4 was prepared as described by Klenk *et al.*<sup>7</sup>, while compound 5 was purchased from Aldrich (Montreal, Quebec, Canada).

#### *General procedure*

The plates were made with silica gel HF<sub>254</sub> (750- $\mu\text{m}$  thickness) using a Desaga TLC applicator, after which they were allowed to air dry for 24 h before use. Chromium trioxide (1 g) was dissolved in water (5 ml) and diluted to 100 ml with glacial acetic acid. Plates were spotted with the appropriate amount of compound (see Table I), developed 15 cm, air dried and sprayed with aqueous acetic acid-chromium trioxide solution. Thiols appeared almost immediately as blue-green spots on a yellowish brown background. Unchlorinated sulfides and sulfinic acid esters appeared after 15-30 min as blue-green spots on a yellowish brown background.  $\alpha$ -Polychlorosulfides and sulfoxides appeared as pale blue spots on a greenish yellow background after vigorous heating.

TABLE I

## RESULTS FOR THIOLS, SULFIDES, SULFOXIDES AND SULFINATE ESTERS

All compounds gave pale blue-green spots on greenish yellow (H) or brown-yellow (RT) background.

No.	Compound	Solvent	Temperature*	R <sub>F</sub>	Amount applied (μg/spot)
<b>Thiols</b>					
1	3-Mercaptopropionic acid	Chloroform	RT	0.18	35
2	Benzenethiol	Carbon tetrachloride	RT	0.62	50
3	Benzylthiol	Chloroform	RT	0.91	53
4	Diphenylmethanethiol	Benzene	RT	0.95	58
5	Triphenylmethanethiol	Benzene	RT	0.95	110
<b>Sulfides</b>					
6	Di- <i>n</i> -butyl	Carbon tetrachloride	RT	0.60	90
7	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ·S·CHCl(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	Carbon tetrachloride	RT	0.72	101
8	Phenyl trichloromethyl	Carbon tetrachloride	H	0.79	115
9	Phenyl chloromethyl	Carbon tetrachloride	RT	0.49	100
10	Phenyl methyl	Carbon tetrachloride	RT	0.74	108
11	Thiacyclopentane	Carbon tetrachloride	RT	0.45	95
12	Bischloromethyl	Benzene	H	0.82	168
13	Methyl trichloromethyl	Benzene	H	0.89	250
14	Methyl dichloromethyl	Benzene	H	0.72	200
15	Methyl chloromethyl	Benzene	RT	0.67	108
<b>Sulfoxides</b>					
16	Dimethyl	Acetone	H	0.20	118
17	Di- <i>n</i> -propyl	Acetone	H	0.54	120
18	Methyl chloromethyl	Ethyl acetate	H	0.48	112
19	Methyl dichloromethyl	Diethyl ether	H	0.49	100
20	Methyl trichloromethyl	Chloroform–diethyl ether (4:1)	H	0.62	650
21	Chloromethyl trichloromethyl	Chloroform	H	0.63	1,131
22	Chloromethyl dichloromethyl	Chloroform–diethyl ether (4:1)	H	0.55	571
23	Phenyl trichloromethyl	Chloroform	H	0.61	500
24	Bischloromethyl	Diethyl ether	H	0.51	107
<b>Sulfinate esters</b>					
25	Methylchloromethane	Methanol–chloroform (2:1)	RT	0.75	118
26	Methylbenzene	Chloroform	RT	0.39	110

\* RT = Room temperature; H = vigorous heating.

## RESULTS AND DISCUSSION

Table I depicts the results obtained on a variety of sulfur functional groups including the  $\alpha$ -polychlorinated sulfoxides, which were of primary interest to me.

In contrast to these functional groups, sulfones and sulfonyl chlorides could not be visualized with acetic acid–chromium trioxide spray. Sulfinyl chlorides could be visualized if sprayed prior to developing. However, development of the sulfinyl chlorides led to decomposition so that no useful data could be obtained.

Results on TLC parallel those in solution in that the deep purple color of the reagent is changed upon reaction with the substrate. In solution the reduced chromium

(Cr<sup>3+</sup>) has a deep green color. However, the spots on the TLC plates are blue. This may simply be a concentration effect or alternatively the reaction may be proceeding further on the plates, furnishing Cr<sup>2+</sup> ions, which, in fact, are sky blue.

The chromium trioxide spray has proved to be generally more sensitive than the ammonium hexanitratocerate(IV) spray. In particular, the chromium trioxide has shown itself to be substantially superior for the  $\alpha$ -polychlorosulfoxides varying from 2.5 times more sensitive for the tetrachlorosulfoxide (compound 21) to 6 times more sensitive for the dichlorosulfoxides (compounds 19 and 24). As well as greater sensitivity, the chromium trioxide gives sharper contrast between the spots and the background making it more reliable and convenient. Furthermore, the chromium trioxide spray is much less expensive than the ammonium hexanitratocerate(IV) spray.

The greater oxidizing power of the chromium trioxide provides little advantage for the detection of compounds which are readily oxidized, due to relatively high electron density on sulfur. However, for those compounds which are more difficult to oxidize, as the  $\alpha$ -polychlorosulfoxides are, the chromium trioxide spray is clearly advantageous. It, too, shows a decline in sensitivity for the sulfoxides which contain three and four  $\alpha$ -chlorine atoms, which must result in substantially lower electron density on sulfur.

## CONCLUSIONS

Acetic acid-chromium trioxide solution has been developed as a spray reagent for the detection of  $\alpha$ -polychlorosulfoxides, sulfides, thiols and sulfinate esters on TLC. This spray has proved to be significantly superior to the previously reported ammonium hexanitratocerate(IV) spray, for the detection of  $\alpha$ -polychlorosulfoxides. Neither sulfones nor sulfonyl chlorides can be detected with this spray as would be expected on the basis of the proposed oxidation of the organosulfur compounds.

## ACKNOWLEDGEMENT

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