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Note

New spray for the detection of sulfonyl chlorides

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In pursuing the chlorination of sulfur compounds as our primary research interest, we have encountered a variety of sulfur compounds which could not be visualized on chromatographic plates. In the past, we have reported^{1,2} the development of sprays which facilitate the detection of thiols, sulfides, sulfoxides (particularly α -polychlorosulfoxides) and sulfinate esters. Both hexanitrateammonium cerate(IV)¹ and chromium trioxide² sprays are oxidizing sprays and are therefore unable to detect sulfones or sulfonyl chlorides.

Recently we have developed a method for the preparation of α,α -dichloro- α -sulfonyl sulfonyl chlorides. The desire to characterize these compounds on thin-layer chromatography (TLC) plates along with our longer-standing desire to detect simpler sulfonyl chlorides, which we have been isolating for some time^{3,4}, has led to a search for such a spray.

Potassium iodide has been employed for the detection of compounds containing the sulfinyl group, *i.e.* thiosulfinates and sulfinic acids^{5,6}. The sensitivity of the spray may be enhanced by spraying the plate with starch solution after spraying with iodide, since the iodine-starch complex gives a stronger color than simple molecular iodine⁶.

EXPERIMENTAL

Chemicals

Compounds 1-3 and 13 (see Table I) were prepared by the method we have developed recently⁷; compound 4 was prepared by the method of Opitz⁸; compound 5 was prepared as we have previously outlined⁴; compounds 7, 8 and 11 were prepared by the exhaustive chlorination of the corresponding symmetric sulfides in aqueous acetic acid utilizing the conditions we have developed for the conversion of α -chloro-sulfides to sulfonyl chlorides⁴; compound 12 was prepared as we have described elsewhere⁹.

Compounds 6, 9 and 10 were purchased from Baker Chemicals (Phillipsburg, N.J., U.S.A.). Silica gel GF₂₅₄ was purchased from Merck (Darmstadt, G.F.R.).

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TABLE I

RESULTS FOR SULFONYL CHLORIDES. α -DICHLORO- β -DISULFONES AND SULFENYL CHLORIDES

All compounds gave amber spots on a colorless background at room temperature after development with chloroform. I = Immediate appearance; TF = appearance after 3-5 min.

No.	Compound	Appearance	R _F value	Amount applied (μ g/spot)
<i>Sulfonyl chlorides</i>				
1	CH ₃ -SO ₂ -CCl ₂ -SO ₂ -Cl	I	0.48	115
2	C ₆ H ₅ -SO ₂ -CCl ₂ -SO ₂ -Cl	I	0.63	129
3	ClCH ₂ -SO ₂ -CCl ₂ -SO ₂ -Cl	I	0.69	120
4	CH ₃ -SO ₂ -CH ₂ -SO ₂ -Cl	I	0.04	490
5	Chloromethane	TF	0.91	253
6	Methane	TF	0.53	563
7	Ethane	TF	0.73	437
8	Propane	TF	0.83	500
9	Benzene	TF	0.75	246
10	<i>p</i> -Toluene	TF	0.86	258
11	Benzyl	TF	0.57	590
<i>α-Dichloro-β-disulfones</i>				
12	CH ₃ -SO ₂ -CCl ₂ -SO ₂ -CH ₂ -C ₆ H ₅	TF	0.40	635
<i>Sulfenyl chlorides</i>				
13	CH ₃ -SO ₂ -CCl ₂ -S-Cl	I	0.47	238

General procedure

The plates were made with silica gel GF₂₅₄ (750 μ m thick) using a Desaga TLC applicator. Plates were air dried 24 h before use. The spray reagent was prepared by dissolving sodium iodide (10 g) in acetone (100 ml). Plates were spotted with the appropriate amount of compound (see Table I), developed 15 cm, air dried and sprayed with sodium iodide solution. Amber spots appeared on a colorless background within 5 min of spraying.

RESULTS AND DISCUSSION

For some time, we have been isolating alkanesulfonyl and arylsulfonyl chlorides from reaction mixtures utilizing column and/or preparative TLC without loss of material due to hydrolysis⁷. However, when the α -sulfonyl sulfonyl chloride (compound 3) was developed on preparative TLC plates and isolated it was found to be 21% sulfonyl chloride and 79% ClCH₂-SO₂-CCl₂H^{**}. The presence of the trichlorosulfone indicates that the α,α -dichloro- α -sulfonyl sulfonyl chloride is very sensitive to traces of moisture and hydrolyzes to furnish the sulfone by a new dechlorosulfonylation reaction which we have recently reported in detail⁷. Thus the sensitivity of the spray reagent for compounds 1-3 is some five times greater than is indicated by the amount of material which must be applied to observe a spot after development.

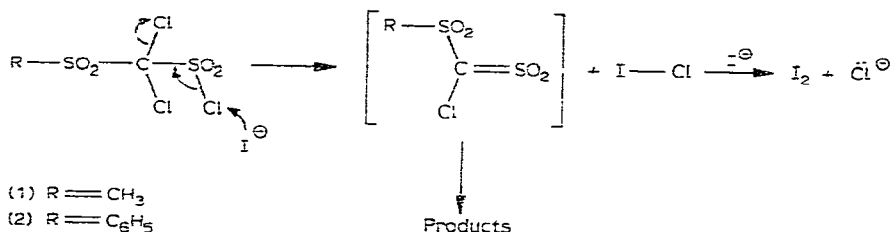
* For example, methanesulfonyl chloride has been quantitatively separated from benzyl chloride by column chromatography⁷.

** Sodium iodide spray does not detect simple α -polychlorosulfones.

Table I depicts the results obtained on the sulfur compounds examined, including the α,α -dichloro- α -sulfonyl sulfonyl chlorides (compounds 1, 2 and 3) which were of primary interest to us. The mode of action of the iodide spray clearly involves reduction of the sulfur compounds. Plates spotted more heavily with compounds 1, 2 and 3 gave black-purple spots and iodine vapour could be observed rising from the surface of the plate.

Two possible pathways for the reduction suggested themselves. Firstly, attack by iodide ion on the chlorine atom attached to sulfur would result in the formation of iodine and the sodium salt of the sulfinic acid. In order to find support for this possibility, we examined a variety of sulfonyl chlorides (compounds 4-11) and found that the results were positive but the sensitivity of the spray was impaired. The second possibility involves attack by iodide ion on one of the chlorine atoms attached to carbon, which would furnish iodine and the α -chloro- α -sulfonyl sulfonyl chloride. We chose to investigate this possibility by examining a compound which contained carbon bound chlorine in a very similar electronic environment, namely the α,α -dichloro- β -disulfone (compound 12). Once again the result was positive although the sensitivity of the spray was impaired.

The results on compound 4 demonstrate that the α -chlorine atoms of compounds 1, 2 and 3 play an important role in the interaction between the spray and these compounds. In order to rationalize the greater sensitivity of the spray and faster appearance of the spots when compounds 1, 2 and 3 are visualized, we are proposing the following mechanism involving both types of chlorine atom:



The intermediacy of a sulfene in a similar reaction has been suggested previously by King and Beatson¹⁰ in 1970.

The superior sensitivity of the spray for chloromethanesulfonyl chloride (compound 5) in comparison with methanesulfonyl chloride (compound 6) is also consistent with the intermediacy of a sulfene for α -chlorosulfonyl chloride substrates.

α,α -Dichloro- α -sulfonyl sulfonyl chlorides have provided new chemistry⁷, new spectrometric properties¹¹ and new behaviour on TLC.

CONCLUSIONS

The development of sodium iodide-acetone solution as a spray reagent for the detection of sulfonyl chlorides has been reported. It reduces the sulfonyl chlorides forming iodine which is visible as an amber spot on the plate. A novel mechanism involving sulfene formation is proposed in order to explain the enhanced sensitivity of the spray for α,α -dichloro- α -sulfonyl sulfonyl chlorides, a new and interesting subclass of sulfur compounds.

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