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Note

A new spray reagent for organosulfur compounds

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In recent years a widespread interest in the preparation, properties and chemistry of α-polyhalosulfoxides has developed[1–12]. During a recent study of the oxidative chlorination of some organosulfur compounds[11,12] we encountered a number of α-polychlorosulfoxides. Attempts to characterize these compounds by thin-layer chromatography (TLC) were initially frustrated by the failure of both phosphomolybdic acid[13] and tetracyanoethylene[14] sprays to visualize the spots.

Thiophenes, thiols, sulfides and disulfides have been reported[15,16] to give colored complexes when added to ammonium hexanitratocerate(IV) solution. Although the thiophene complexes have some stability, the others undergo rapid oxidation, giving rise to colorless solutions.

The addition of an alcohol to ammonium hexanitratocerate(IV) solution results in the formation of a deep red stable complex which is the basis of a qualitative test for organic hydroxyl groups[17,18]. The formation of complexes has been rationalized as depicted below, on the basis of titrimetric evidence.

$$ROH + Ce(NO_3)_6^{2-} \rightarrow Ce(OR)(NO_3)_5^{2-} + H^+ + NO_3^-$$

EXPERIMENTAL

Chemicals

Compounds 1 and 2 (*cf.* Table I) were supplied by Dr. R. W. Frei; compounds 3, 4, 6 and 10 were purchased from Eastman-Kodak (Rochester, N.Y., U.S.A.); compounds 11 and 17 from Fluka (Buchs, Switzerland); and compound 16 was obtained from Fisher Scientific (Fair Lawn, N.J., U.S.A.). Ammonium hexanitratocerate(IV) was obtained from the BDH (Poole, Great Britain). Silica gel HF_{254} was purchased from Merck (Darmstadt, G.F.R.).

Compound 5 was prepared as described by Tsung and Chi[19], compounds 7–9, 12–14 and 17 were prepared as described by Bordwell and Pitt[20], or Truce *et al.*[21]; compounds 19–24 were prepared as we have described elsewhere[12] and compound 18 was prepared as described by Tsuchihashi and Ogura[22].

The appropriate sulfinyl chlorides may be prepared as we have described elsewhere[12]. The sulfinate esters 25 and 26 are prepared by the dropwise addition of the sulfinyl chloride to an excess of cold methanol, followed by stirring at room temperature for 1 h, and distillation at reduced pressure.

General procedure

The plates were made with silica gel HF_{254} (750-μm thickness) using a Desaga TLC applicator. Plates were air dried for 24 h before use. A standard solution of ammonium hexanitratocerate(IV) solution was prepared following the procedure of Shriner *et al.*[18]. Ammonium hexanitratocerate(IV) (40 g) was dissolved in 2 *N* HNO_3 (100 ml). Plates were spotted with the appropriate amount of compound (see Table I), developed 15 cm, air dried, and sprayed with ammonium hexanitratocerate(IV) solution. Spots for the non-sulfoxides appeared almost immediately as colorless areas on a yellow background. The α-polychlorosulfoxide spots required vigorous heating on a hot plate in order to be visualized as yellow-brown areas on a colorless background.

TABLE I

RESULTS FOR THIOLS, SULFIDES, SULFOXIDES, AND SULFINATE ESTERS

No.	*Compound*	*Solvent*	*Color**	*Temp.***	R_F	*μg/spot*
	Thiols					
1	2-Benzimidazolethiol	EtOAc	C	RT	0.89	80
2	2-Mercaptonaphthalene	$CHCl_3$	C	RT	0.83	92
3	3-Mercaptopropionic acid	$CHCl_3$	C	RT	0.18	70
4	Benzenethiol	CCl_4	C	RT	0.62	80
5	Benzylthiol	$CHCl_3$	C	RT	0.91	82
	Sulfides					
6	Di-*n*-butyl	CCl_4	C	RT	0.60	85
7	$CH_3(CH_2)_3$-S-CHCl$(CH_2)_2CH_3$	CCl_4	C	RT	0.72	88
8	Phenyl trichloromethyl	CCl_4	C	RT	0.79	90
9	Phenyl chloromethyl	CCl_4	C	RT	0.49	87
10	Phenyl methyl	CCl_4	C	RT	0.74	89
11	Thiacyclopentane	CCl_4	C	RT	0.45	90
12	Bischloromethyl	C_6H_6	C	RT	0.82	100
13	Methyl trichloromethyl	C_6H_6	C	RT	0.89	95
14	Methyl dichloromethyl	C_6H_6	C	RT	0.72	90
15	Methyl chloromethyl	C_6H_6	C	RT	0.67	90
	Sulfoxides					
16	Dimethyl	Acetone	YB	H	0.20	90
17	Di-*n*-propyl	Acetone	YB	H	0.54	92
18	Methyl chloromethyl	EtOAc	YB	H	0.48	200
19	Methyl dichloromethyl	Et_2O	YB	H	0.49	600
20	Methyl trichloromethyl	$CHCl_3$–Et_2O(4:1)	YB (wk)	H	0.62	1,630
21	Chloromethyl trichloromethyl	CHCl	YB (wk)	H	0.63	2,820
22	Chloromethyl dichloromethyl	$CHCl_3$–Et_2O(4:1)	YB	H	0.55	1,630
23	Phenyl trichloromethyl	$CHCl_3$	YB	H	0.61	1,300
24	Bischloromethyl	Et_2O	YB	H	0.51	600
	Sulfinate esters					
25	Methyl chloromethane	MeOH–$CHCl_3$(2:1)	C	RT	0.75	250
26	Methyl benzene	$CHCl_3$	C	RT	0.39	200

* Abbreviations of colors: C = colorless; YB = yellow brown; (wk) = weakly developed.

** H = vigorous heating; RT = room temperature.

RESULTS AND DISCUSSION

Table I depicts the results obtained on a variety of sulfur functional groups including the α-polychlorosulfoxides, which were of primary interest to us.

In contrast to these functional groups, sulfones and sulfonyl chlorides could not be visualized with ammonium hexanitratocerate(IV) spray. Sulfinyl chlorides could be readily 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. Unchlorinated sulfoxides give intensely red, stable complexes when added directly to ammonium hexanitratocerate(IV) solution. On the plates unchlorinated sulfoxides give orange-brown spots upon spraying. However, α-chlorinated sulfoxides (with the exception of chloromethyl methyl sulfoxide) fail to give the red complex or any sign of reaction at room temperature. The same results are realized on TLC unless the plates are vigorously heated (after spraying). After vigorously heating the plates yellow-brown spots appear on a colorless background.

Sulfides, thiols and sulfinate esters give colorless spots on a yellow background without heating. In solution the yellow reagent goes colorless in a vigorously exothermic reaction immediately upon addition of a sulfide, thiol or sulfinate ester. Such an observation, coupled with the absence of change when sulfones or sulfonyl chlorides are added to a solution of the reagent, is consistent with the proposal of an oxidation–reduction reaction as originally advanced by Hartough[16].

In general, one would anticipate that oxidation would proceed with more difficulty as the electron density on the sulfur atom was decreased, thereby impairing the sensitivity of an oxidizing spray such as ammonium hexanitratocerate(IV). Apparently, simply incorporating chlorine atoms on the carbon atom α to the sulfur atom (see sulfides in Table I), or an oxygen atom on the sulfur atom (see dimethyl sulfoxide and di-*n*-propyl sulfoxide in Table I) does not sufficiently reduce the electron density on the sulfur atom to alter the sensitivity of the spray. However, the presence of both chlorine atoms on the α carbon atoms and an oxygen atom on sulfur significantly reduces the electron density on the sulfur atom, thus substantially impairing the sensitivity of the spray, as expected (see compounds 18–24 in Table I).

CONCLUSIONS

The development of ammonium hexanitratocerate(IV) solution as a spray reagent for the detection of selected organosulfur compounds has been reported. It is believed to oxidize the organosulfur compounds which is more difficult in the case of sulfoxides due to the formation of stable complexes. Vigorous heating decomposes the complexes and permits the oxidation to occur, thereby providing a means to detect α-polyhalosulfoxides, a relatively new and interesting class of compounds.

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