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Note

Selective detection of sulphoxides and sulphimides by thin-layer chromatography using trifluoroacetic anhydride–sodium iodide as a reagent

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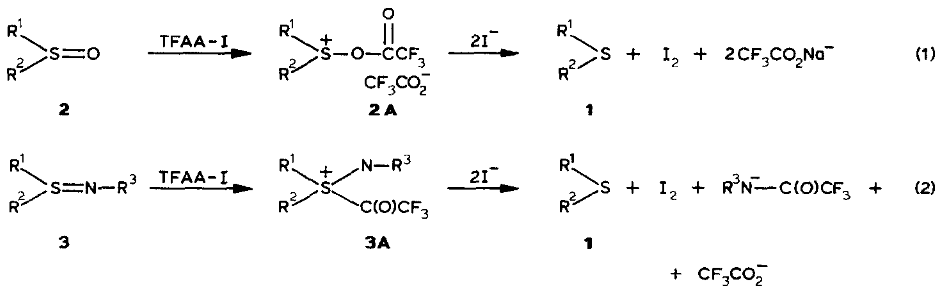
Sulphoxides and sulphimides are important intermediates in organic synthesis[1,2]. Morever, this group of organosulphur compounds also shows very interesting biological activity[3,4]. For this reason their detection and quantitation are of interest[5,6]. Their thin-layer chromatographic (TLC) detection, however, is limited to a narrow range of spray reagents. Thus, hydriodic acid[7], iodobismuthate solution[8] and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) solution[9] were introduced as spray reagents for certain sulphoxides. Later, acetic acid–chromium trioxide solution[10] and very recently the Dragendorff reagent[11] were applied.

Recently it was shown by us[12,13] that trifluoroacetic anhydride–sodium iodide (TFAA-I) brings about the quantitative deoxygenation of sulphoxides (2) and sulphimides (3) to the corresponding sulphides (1), according to eqns. 1 and 2 and is not able to reduce sulphones (4) and sulphoximides (5).



Because in the reactions 1 and 2 stoichiometric amounts of elemental iodine are formed, these procedures have been adapted for microdeterminations of sulphoxides and sulphimides[14,15]. In this paper we present our findings on the application of TFAA-I to the detection of sulphoxides (2) and sulphimides (3) in TLC systems.

EXPERIMENTAL

Materials

Trifluoroacetic anhydride (TFAA), dimethyl sulphoxide (2a), dibutyl sulphoxide (2c) and diphenyl sulphoxide (2k) were obtained from Aldrich. The other sulphoxides were prepared by the oxidation of the corresponding sulphides either with hydrogen peroxide in methanol solution[16]or with bromine in a two-phase system[17]. The sulphimides[18], sulphones[19] and sulphoxyimides[20] were prepared by standard procedures.

Solutions

A 0.5 *M* solution of sodium iodide in anhydrous acetone and a 0.8 *M* solution of TFAA in anhydrous acetone (prepared immadiately before use) were employed. The concentration of the compounds chromatographed were approximately $5 \cdot 10^{-2}$–10^{-3} *M* in anhydrous acetone. The Dragendorff reagent comprised a 2% solution of potassium bismuth tetraiodide in 0.01 *M* hydrochloric acid[9], the DDQ reagent a 2% solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in benzene[10] and the chromium trioxide reagent an 1% solution of chromium trioxide in 95% acetic acid.

TABLE I

DETECTION LIMITS FOR SULPHOXIDES (2) AND SULPHIMIDES (3) USING TFAA-I AS THE DETECTION REAGENT

Me = Methyl; Et = ethyl; Pr = propyl; Bu = butyl; Ph = phenyl; Tos = tosyl.

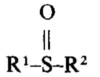
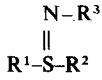
No.	*Structure*	*R^1*	*R^2*	*R^3*	*Detection limit*		*TLC R_F value (acetone, silica)*
					µg	*µmol*	
2a	 $R^1\text{-}\overset{\overset{O}{\|}}{S}\text{-}R^2$	Me	Me		0.30	0.0038	0.10
2b		Me	Bu		1.06	0.0088	0.20
2c		Bu	Bu		0.88	0.0054	0.52
2d		Me	$PhCH_2$		0.74	0.0048	0.33
2e		Pr	$PhCH_2$		1.12	0.0061	0.50
2f		$PhCH_2$	$PhCH_2$		1.08	0.0047	0.64
2g		*p*-$CH_3C_6H_4$	Et		1.58	0.0094	0.54
2h		*p*-$CH_3C_6H_4$	*n*-Pr		1.28	0.007	0.61
2i		Ph	*tert.*-Bu		1.1	0.006	0.59
2j		Ph	*p*-$CH_3C_6H_4$		1.78	0.008	0.64
2k		Ph	Ph		5.0	0.024	0.58
2l		Ph	*o*-$CH_3OC_6H_4$		5.0	0.022	0.62
3a	 $R^1\text{-}\overset{\overset{N-R^3}{\|}}{S}\text{-}R^2$	Ph	Me	Tos	2.8	0.0095	0.57
3b		*p*-$CH_3C_6H_4$	Me	Tos	9.4	0.032	0.61

TABLE II

RESULTS OF THE REACTION OF TFAA-I WITH DIPHENYL SULPHIDE (1k), DIPHENYL SULPHONE (4k) AND SULPHOXIMIDE (5a) ON TLC PLATES

No.	*Structure*	*R*¹	*R*²	*R*³	*Amount taken (μg)*	*Detection on alumina*				*Detection on silica*			
						R_F	*UV*	I_2	*TFAA-I*	R_F	*UV*	I_2	*TFAA-I*
					10		–	–	–		–	–	–
1k	$R^1\text{–}S\text{–}R^2$	Ph	Ph		50	0.77	+	+	–	0.70	+	+	–
					100		+	++	–		+	++	–
2k	$R^1\text{–}\overset{\overset{\displaystyle O}{\Vert}}{S}\text{–}R^2$	Ph	Ph		10	0.66	–	–	++	0.58	–	–	++
					10		–	–	–		–	–	–
4k	$R^1\text{–}\overset{\overset{\displaystyle O}{\Vert}}{\underset{\underset{\displaystyle O}{\Vert}}{S}}\text{–}R^2$	Ph	Ph		50	0.77	+	+	–	0.68	+	+	–
					100		+	+	–		+	++	–(+)*
					10		–	–/+	–		–	–/+	–
5a	$R^1\text{–}\overset{\overset{\displaystyle O}{\Vert}}{\underset{\underset{\displaystyle N\text{–}R^3}{\Vert}}{S}}\text{–}R^2$	Me	Ph	H	50	0.52	–	+	–/+**	0.39	–	+	–
					100		–	+	–/+**		–	+	–

* A spot of iodine appeared after 1 h of exposition.

** After 2 h of exposive.

TLC

Pre-coated silica gel 60 F_{254} aluminium sheets (10 cm × 5 cm), 0.2 mm thick (Merck), were used for TLC. The plates were spotted with the appropriate amount of compound (see Tables), developed for 8 cm with acetone, air dried and sprayed with sodium iodide solution and subsequently with TFAA solution. Sulphoxides (2) and sulphimides (3) appeared almost immediately as brown spots on a white background, and are stable for more than 20 min.

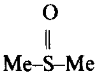
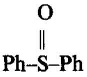
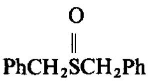
RESULTS AND DISCUSSION

The results of the application of the TFAA-I reagent for visualization of sulphoxides (2) and sulphimides (3) on TLC plates are summarized in Table I. The detection of compounds 2 and 3 on TLC plates after reaction with TFAA-I is very rapid the spots of iodine being formed immediately after spraying with the reagent. The corresponding detection limits (Table I) were found to be dependent on the structures: thus dialkyl sulphoxides (2a–i) at 4–9 nmol and diaryl sulphoxides (2j–l) at 10–25 nmol. The detection limits of sulphimides 3 were in the range 10–25 nmol.

The results collected in Table II clearly indicate that this procedure allows the selective detection of sulphoxides (2) and sulphimides (3) in the presence of sulphides, sulphones and sulphoximides. Diphenyl sulphide (1k), diphenyl sulphone (3k) and phenyl methyl sulphoximide (5a) do not react with the reagent and do not interfere

TABLE III

COMPARISON OF REAGENTS FOR THE DETECTION OF SULPHOXIDES BY TLC

Sulphoxide	*Amount applied (µg/spot)*	*Detection reagent*			
		Bi(III)-KI[8]	*DDQ-BH$_3$*[9]	*CrO$_3$-acetic acid*[10]	*TFAA-I*[*]
 $\mathrm{Me{-}\overset{\overset{O}{\|}}{S}{-}Me}$	1	–	–	–	+
	5	–	–	–	+
	25	–	–	–	+
	74	–	+/–**	+***	+
	150	–	+	+	+
 $\mathrm{Ph{-}\overset{\overset{O}{\|}}{S}{-}Ph}$	1	–	–	–	+/–
	5	–	–	–	+
	25	+/–§	–	–	+
	91	+	–	+***	+
	181	+§	+**	+	+
 $\mathrm{PhCH_2\overset{\overset{O}{\|}}{S}CH_2Ph}$	1	–	–	–	+
	5	–	–	–	+
	25	–	–	–	+
	100	+§	+**	+***	+
	200	+	+	+	+

* This paper.

** According to ref. 9 the detection limits for dialkyl and diaryl sulphoxides are 5–10 µg.

*** According to ref. 10, dimethyl sulphoxide was detectable at 118 µg.

§ According to ref. 8 the detection limits are: dimethyl sulphoxide, no reaction, dipropyl sulphoxide, 33 µg; dibutyl sulphoxide, 110 µg. According to ref. 11. The detection limits are: phenyl ethyl sulphoxide and phenyl benzyl sulphoxide, 35–36 µg.

in the test, even at the level of 100 μg of compounds in the spot. The present reagent (see Table III) has proved to be significantly more sensitive than the previously reported sprays[8–11] for the detection of sulphoxides.

Attempts to modify the TFAA-I spray by replacement of sodium iodide with lithium bromide as well as the use of starch indicator for intensification of the iodine spots did not improve the detectability of sulphoxides and sulphanilimides.

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