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THIN-LAYER AND GAS-LIQUID CHROMATOGRAPHY OF
DERIVATIVES OF ISOMERIC CHLOROPHENOLSCHLOROPHENYL FLUROSULFONYL-BENZENESULFONATES AND
RELATED COMPOUNDS

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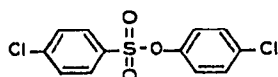
SUMMARY

The thin-layer and gas-liquid chromatography of derivatives of the isomeric chlorophenols, *e.g.* the isomeric chlorophenyl fluorosulfonyl-benzenesulfonates, were compared with the respective precursor isomeric fluorosulfonyl-benzenesulfonyl chlorides and acaricidal chlorophenyl benzenesulfonates. The thin-layer chromatographic investigation utilized four solvent systems and five electron-acceptor reagents to separate and distinguish the various isomeric derivatives. Gas-liquid chromatography was best accomplished using 5% OV-17 and SE-30 with flame ionization detection.

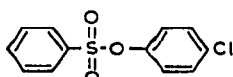
INTRODUCTION

Isomeric chlorophenols and their esters are important environmental agents that are extensively used as insecticides¹, herbicides^{2,3}, growth regulators^{4,5}, nematocides^{6,7}, germicides⁸ and as fungicides in many industries including the textile, leather, paint and adhesive manufacturing processes.

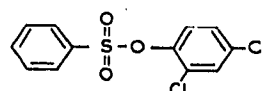
Chlorophenols such as *p*-chlorophenol and 2,4-dichlorophenol are also hydrolysis products of the acaricides ovex (*p*-chlorophenyl *p*-chlorobenzenesulfonate) (I), fenson (*p*-chlorophenyl benzenesulfonate) (II) and genite (2,4-dichlorophenyl benzenesulfonate) (III), respectively.



(I)



(II)



(III)

Earlier papers have described the detection and thin-layer (TLC) and gas-liquid chromatography (GLC) of a number of derivatives of isomeric chlorophenols, e.g., N-(trichloroacetyl) carbamates^{9,10} and *m*-fluorosulfonyl-benzoate esters¹¹.

The purpose of this investigation was to elaborate further the effect of structure on TLC and GLC behavior of additional derivatives of the isomeric monochlorophenols, e.g., the isomeric chlorophenyl fluorosulfonyl-benzenesulfonates as well as to compare their chromatographic behavior with precursor isomeric fluorosulfonyl-benzenesulfonyl chlorides and related derivatives such as the acaricides ovex and genite.

EXPERIMENTAL

Materials

Detecting reagents were: (1) DDQ reagent: 2% 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in benzene¹²; (2) TCNE reagent: 2% tetracyanoethylene in benzene¹²; (3) Gibbs' reagent: 2% 2,6-dibromo-N-chloro-*p*-benzoquinoneimine in benzene; (4) TNF reagent: 2% 2,4,7-trinitrofluorenone in benzene; (5) Chloranil: 1% tetrachloro-*p*-benzoquinone in benzene.

The developing solvents utilized were: (a) 2.5% acetone in benzene; (b) chloroform-acetic acid (5:1); (c) toluene-ethyl acetate (1:1); and (d) 5% ethylene dichloride in benzene.

The chlorophenyl *o*-, *m*- and *p*-fluorosulfonyl-benzenesulfonates were prepared via the reaction of the respective fluorosulfonyl-benzenesulfonyl chloride with the isomeric monochlorophenols in benzene and triethylamine for 1 h at 85° and the product recrystallized from benzene-acetone (3:1). The isomeric fluorosulfonyl-benzenesulfonyl chlorides and chlorophenols were obtained from Aldrich Chemical Co., Milwaukee, Wisc., U.S.A.; the pesticidal acaricides ovex and genite from the Pesticides Research Laboratory, Perrine, Fla., U.S.A.; the detecting reagents 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 2,6-dibromo-N-chloro-*p*-benzoquinoneimine, and tetrachloro-*p*-benzoquinone from J. T. Baker Corp., Phillipsburg, N.J., U.S.A.; and tetracyanoethylene and 2,4,7-trinitrofluorenone from Distillation Industries, Rochester, N.Y., U.S.A.

Thin-layer chromatography

*Chromatoplates prepared according to MORLEY AND CHIBA*¹³. Silica Gel DF-5* was applied on 8 × 8 in. plates to a thickness of 280 μ. After air-drying, the plates were activated in an oven for 30 min. Acetone solutions (1–2 μl containing 1–10 μl of test substance) were applied along a line 2.5 cm from the lower end of the plate and developed by the ascending method. After evaporation of the solvent, the spots were located on the plate by UV detection, then sprayed with one of the chromogenic reagents and the initial color development as well as subsequent color changes noted.

Pre-coated sheets. MN-Polygram SILN-HR/UV₂₅₄ (Brinkmann) precoated silica gel 20 × 20 cm sheets were used without further activation.

Gas-liquid chromatography

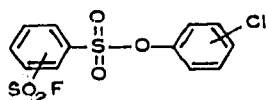
The following gas chromatographs were employed: (1) Varian Model 1200 equipped with a flame ionization detector and a 5 ft. × 1/8 in. O.D. stainless steel column

* Obtained from Camag, Muttenz, Switzerland.

coated with 3% SE-30 on 100/120 mesh Varoport 30 and a 10 ft. \times $\frac{1}{8}$ in. O.D. stainless steel column coated with 10% OV-1 on 80/100 mesh Supelcoport; (2) Hewlett-Packard Model 700-1099F equipped with a flame ionization detector and a 6 ft. \times $\frac{1}{8}$ in. I.D. stainless steel column coated with 5% OV-17 on 80/100 Supelcoport; and (3) Hewlett-Packard Model 5750 equipped with both flame ionization and ^{63}Ni electron-capture detectors and (a) 6 ft. \times $\frac{1}{4}$ in. O.D. spiral glass containing 4.9% OV-17 on 100/120 mesh Gas-Chrom Q; (b) 6 ft. \times $\frac{1}{8}$ in. O.D. stainless steel coated with 3% OV-1 on 100/120 mesh Gas-Chrom Q columns. Standard derivative solutions were prepared in benzene in concentrations of 1 mg/ml. Specific analytical operating conditions are given in Table IV.

TABLE I

$R_F \times 100$ VALUES OF ISOMERIC CHLOROPHENYL FLUOROSULFONYL-BENZENESULFONATES ON SILICA GEL DF-5 CHROMATOPLATES AND MN-POLYGRAM SILN-HR/UV₂₅₄ PRE-COATED SHEETS



Solvents: (A) 2.5% acetone in benzene, (B) chloroform-acetic acid (5 : 1), (C) toluene-ethyl acetate (1 : 1), and (D) 5% ethylene dichloride in benzene.

Compound No.	Derivatives	M.p. ($^{\circ}\text{C}$)	Silica Gel DF-5				MN-Polygram SILN-HR/UV ₂₅₄			
			A	B	C	D	A	B	C	D
<i>Chlorophenyl o-fluorosulfonyl-benzenesulfonates</i>										
1	<i>o</i> -Chlorophenyl	145-147	38	46	12	31	34	48	15	28
2	<i>m</i> -Chlorophenyl	87-89	44	51	18	39	41	54	20	34
3	<i>p</i> -Chlorophenyl	140-142	56	57	25	45	51	59	27	41
<i>Chlorophenyl m-fluorosulfonyl-benzenesulfonates</i>										
4	<i>o</i> -Chlorophenyl	157-159	45	53	10	37	40	57	16	30
5	<i>m</i> -Chlorophenyl	149-151	53	58	15	44	46	61	20	36
6	<i>p</i> -Chlorophenyl	161-162	64	62	21	52	54	66	26	45
<i>Chlorophenyl p-fluorosulfonyl-benzenesulfonates</i>										
7	<i>o</i> -Chlorophenyl	186.5-187.5	60	57	31	60	57	60	35	55
8	<i>m</i> -Chlorophenyl	192-194	67	61	38	66	65	65	41	61
9	<i>p</i> -Chlorophenyl	226-228	77	66	46	74	74	70	48	69

RESULTS AND DISCUSSION

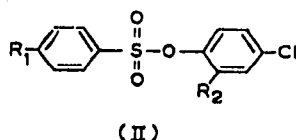
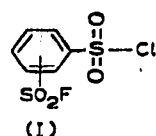
Thin-layer chromatography

Tables I and II depict the $R_F \times 100$ values of the isomeric chlorophenyl fluorosulfonyl-benzenesulfonates, fluorosulfonyl-benzenesulfonyl chlorides and acaricidal chlorophenyl benzenesulfonates, respectively, on Silica Gel DF-5 plates and pre-coated Polygram sheets developed in four solvent systems, *e.g.*, (a) 2.5% acetone in benzene, (b) chloroform-acetic acid (5:1), (c) toluene-ethyl acetate (1:1), and (d) 5% ethylene dichloride in benzene.

The isomeric chlorophenyl sulfonate derivatives as well as the precursor fluorosulfonyl-benzenesulfonyl chlorides were separated without decomposition in all of the solvent systems employed. The 2.5% acetone in benzene system was the solvent of

TABLE II

$R_F \times 100$ VALUES OF ISOMERIC FLUOROSULFONYL-BENZENESULFONYL CHLORIDES (I) AND ACARICIDAL CHLOROPHENYL BENZENESULFONATES (II) ON SILICA GEL DF-5 CHROMATOPLATES AND MN-POLYGRAM SILN-HR/UV₂₅₄ PRE-COATED SHEETS



Solvents: (A) 2.5% acetone in benzene, (B) chloroform-acetic acid (5:1), (C) toluene-ethyl acetate (1:1), and (D) 5% ethylene dichloride in benzene.

Compound No.	Derivatives	M.p. (°C)	Silica Gel DF-5				MN-Polygram SILN-HR/UV ₂₅₄			
			A	B	C	D	A	B	C	D
<i>Fluorosulfonyl-benzenesulfonyl chlorides</i>										
10	<i>o</i> -Fluorosulfonyl	88-89	48	80	39	45	42	85	43	40
11	<i>m</i> -Fluorosulfonyl	110-112	60	85	44	61	51	91	48	49
12	<i>p</i> -Fluorosulfonyl	156-158 5 mm	71	91	52	74	63	97	56	62
<i>Acaricidal chlorophenyl benzenesulfonates</i>										
13	Ovex (R ₁ = Cl; R ₂ = H)	86.5-87	70	86	53	61	66	80	60	52
14	Genite (R ₁ = H; R ₂ = Cl)	42-43	64	81	47	50	58	74	52	40

TABLE III

COLOR COMPLEXES FORMED ON SILICA GEL DF-5 WITH ELECTRON-ACCEPTOR REAGENTS

Designation of colors: Bg = beige, Bn = brown, Gr = grey, M = maroon, O = orange, P = purple, R = rose, T = tan, V = violet, and Y = yellow.

Compound No.	Derivatives	Detecting reagents				
		DDQ	TCNE ^a	Gibbs'	TNF	Chloranil
<i>Chlorophenyl o-fluorosulfonyl-benzenesulfonates</i>						
1	<i>o</i> -Chlorophenyl	R→P	O-Y	Bg→T	T→Bn	R→V
2	<i>m</i> -Chlorophenyl	R→P	O-Y	Bg→T	T→Bn	R→V
3	<i>p</i> -Chlorophenyl	P	O	O-Bn	Bn	V
<i>Chlorophenyl m-fluorosulfonyl-benzenesulfonates</i>						
4	<i>o</i> -Chlorophenyl	R→P	O-Y	T	Bn	Bn→V
5	<i>m</i> -Chlorophenyl	R→P	O	T	Bn	Bn→V
6	<i>p</i> -Chlorophenyl	P	O	O-Bn	Bn	V
<i>Chlorophenyl p-fluorosulfonyl-benzenesulfonates</i>						
7	<i>o</i> -Chlorophenyl	Bn→P	O-Y	T	T→Bn	Bn-V
8	<i>m</i> -Chlorophenyl	Bn→P	O-Y	T	Bn	Bn-V
9	<i>p</i> -Chlorophenyl	P	O	O-Bn	Bn	V
<i>Fluorosulfonyl-benzenesulfonyl chlorides</i>						
10	<i>o</i> -Fluorosulfonyl	Bn→M	O	Bg→T	Y	T
11	<i>m</i> -Fluorosulfonyl	Bn→M	O	Bg→T	Y	T
12	<i>p</i> -Fluorosulfonyl	M	O	T	Y	Bn
<i>Acaricidal chlorophenyl benzenesulfonates</i>						
13	Ovex	Y	O	Gr	Bn-V	Y-Gr
14	Genite	Y	O	Gr	Bn-V	Y-Gr

^a Colors after exposure to ammonia vapors (2 min).

choice in the former case while 5% ethylene dichloride in benzene resolved the latter derivatives as well as the acaricides ovex and genite most efficiently. The order of R_F values for both series of isomeric derivatives was $p > m > o$ in all of the solvent systems.

Table III depicts the color complexes formed on Silica Gel DF-5 with electron-acceptor reagents. A number of general observations can be made as to the reactivity of the various classes of derivatives. Both the isomeric chlorophenyl fluorosulfonyl-benzenesulfonates and the acaricidal chlorophenyl benzenesulfonates are more reactive than the fluorosulfonyl-benzenesulfonyl chlorides toward all of the reagents screened, *e.g.*, the above two classes yield colors (from instant to 5 min), whereas the fluorosulfonyl-benzenesulfonyl chlorides are generally detected after 15 min or require development at 80°. It is of interest to note that in earlier work¹⁴ sulfoxides were found to be more reactive than sulfones. The latter are weaker bases (poorer donors) due to the net decrease in the electron density on the sulfur and oxygens. A comparison of the class formulas (Tables I and II) suggests that analogously, the fluorosulfonyl-benzenesulfonyl chlorides are poorer donors than the oxygen-enriched chlorophenyl fluorosulfonyl-benzenesulfonates.

Table III also indicates that it is possible to distinguish the various classes of derivatives studied using a number of detecting reagents. For example, utilizing the DDQ reagent, the isomeric chlorophenyl fluorosulfonyl-benzenesulfonates, fluorosulfonyl-benzenesulfonyl chlorides and the acaricidal chlorophenyl benzenesulfonates formed purple, maroon and yellow spots, respectively, on a light tan background. The lower limits of detection for the above categories were 2, 4 and 1 μg per spot with the DDQ reagent. Similarly, chloranil and Gibbs' reagent permitted facile differentiation of the same three tested categories of derivatives with limits of detection in the order of 2, 4, 2 for chloranil and 3, 5 and 3 μg per spot for Gibbs' reagent, respectively. The use of TCNE reagent followed by exposure of the chromatoplates to ammonia yielded orange or orange-yellow spots for all the derivatives, with detection in the order of 5 μg per spot. The TNF reagent was least sensitive, with detection of all derivatives in the order of approx. 6–10 μg per spot. The substituted *p*-benzoquinone-type detectors, *e.g.*, DDQ and chloranil (detectors 1 and 5) were more sensitive than the halogenated quinoneimine detector (Gibbs' reagent, detector 3). The overall utility of the electron-acceptor reagents toward the classes of derivatives studied was: DDQ, chloranil > Gibbs' > TCNE > TNF.

With regard to steric effects in the series of isomeric chlorophenyl fluorosulfonyl-benzenesulfonates and fluorosulfonyl-benzenesulfonyl chlorides, the reactivity of these derivatives with the electron-acceptor reagents was generally in the order of $p > m > o$; *e.g.*, the respective *para* isomers (compounds 3, 6, 9 and 12) yielded instant colors, whereas the *meta* isomers (compounds 2, 5, 8 and 11) after 1–2 min and the *ortho* isomers (compounds 1, 4, 7 and 10) yielded colors only after approx. 5 min with somewhat decreased sensitivity.

The use of pre-coated silica gel sheets (MN-Polygram SILN-HR/UV₂₅₄, Brinkmann) permitted the UV detection of the above classes of compounds in amounts of approximately 5 μg per spot.

Gas chromatography

Five different procedures were surveyed in performing the analysis. For each

TABLE IV
GAS CHROMATOGRAPHIC PARAMETERS

		Determination				
		A	B	C	D	E
Instrument		Hewlett-Packard Model 700-1099F	Varian Model 1200	Varian Model 1200	Hewlett-Packard Model 5750	Hewlett-Packard Model 5750
Detector and temperature		Flame ionization; 290°	Flame ionization; 230°	Flame ionization; 230°	Electron-capture (⁶³ Ni); 255°	Flame ionization; 260°
Column		Spiral of stainless steel; 6 ft. × 1/8 in. I.D.; packing: 5% OV-17 on 80/100 mesh Supelcoport	Spiral of stainless steel; 5 ft. × 1/8 in. O.D.; packing: 3% SE-30 on 100/120 mesh Varoport 30	Spiral of stainless steel; 10 ft. × 1/8 in. O.D.; packing: 10% OV-1 on 80/100 mesh Supelcoport	Spiral glass 6 ft. × 1/4 in. O.D.; packing: 4.9% OV-17 on 100/120 mesh Gas-Chrom Q	Spiral of stainless steel 6 ft. × 1/8 in. O.D.; packing: 3% OV-1 on 100/120 mesh Gas-Chrom Q
Column temperature		225°	200°	200°	240°	Programmed to 160° for 3 min; then 15°/min to 240°
Injector temperature		260°	250°	250°	255°	280°
Carrier gas		Helium, 50 ml/min	Helium, 20 ml/min	Helium, 20 ml/min	Helium, 70 ml/min; 5% methane in argon purge	Helium, 50 ml/min
Recorder and paper speed		Model Hro-7127A strip chart; 0.25 in./min	Sargeant-Weich Model SRLG; 0.25 in./min	Sargeant-Weich Model SRLG; 0.25 in./min	Model 7128A strip chart; 0.25 in./min	Model 7128A strip chart; 0.25 in./min
Attenuation		5 × 10 ²	8 × 10 ²	8 × 10 ²	8 × 10 ²	8 × 10 ²

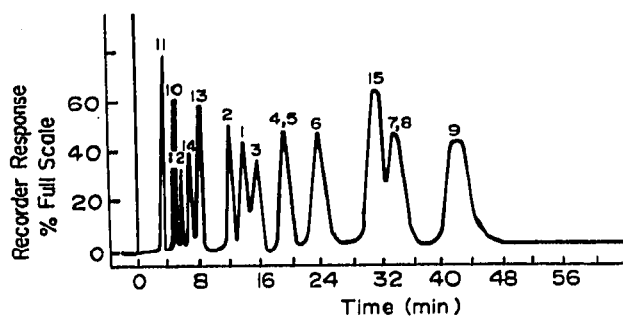


Fig. 1. Separation of the components of the isomeric chlorophenyl fluorosulfonyl-benzenesulfonates, fluorosulfonyl-benzenesulfonyl chlorides and acaricides on 5% OV-17 at 225°. The numbering of the peaks corresponds to that in Table V.

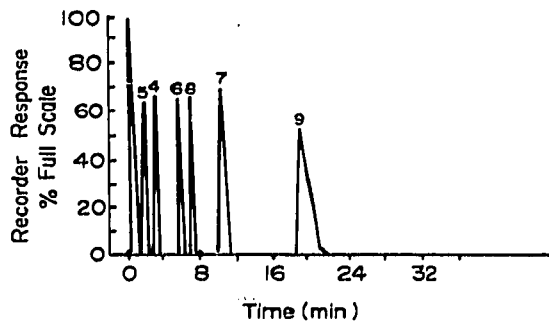


Fig. 2. Separation of the isomeric chlorophenyl *m*- and *p*-fluorosulfonyl-benzenesulfonates on 3% SE-30 at 200°. The numbering of the peaks corresponds to that in Table V.

TABLE V

GAS CHROMATOGRAPHY OF ISOMERIC CHLOROPHENYL FLUROSULFONYL-BENZENESULFONATES, FLUROSULFONYL-BENZENESULFONYL CHLORIDES AND ACARICIDES

Compound No.	Derivatives	Retention times (min) ^a				
		A ^b	B	C	D	E
<i>Chlorophenyl o</i> -fluorosulfonyl-benzenesulfonates						
1	<i>o</i> -Chlorophenyl	15.01	3.36	8.6	<u>11.05</u> [6.45, 13.6]	11.24
2	<i>m</i> -Chlorophenyl	13.96	2.94	8.0	10.19	11.20
3	<i>p</i> -Chlorophenyl	15.87	4.60	10.5	12.01 [2.04, 5.13]	11.53
<i>Chlorophenyl m</i> -fluorosulfonyl-benzenesulfonates						
4	<i>o</i> -Chlorophenyl	19.78	3.65	10.0	10.02	11.21
5	<i>m</i> -Chlorophenyl	19.70	2.35	8.3	9.38	11.00
6	<i>p</i> -Chlorophenyl	24.00	6.34	10.2	5.05 [2.61, 11.19]	11.74
<i>Chlorophenyl p</i> -fluorosulfonyl-benzenesulfonates						
7	<i>o</i> -Chlorophenyl	35.10	10.67	12.65	11.57	—
8	<i>m</i> -Chlorophenyl	35.00	7.17	12.01	5.32 [2.61, 11.9]	—
9	<i>p</i> -Chlorophenyl	42.00	19.43	22.15	5.41 [2.22, 11.80]	—
<i>Fluorosulfonyl-benzenesulfonyl chlorides</i>						
10	<i>o</i> -Fluorosulfonyl-	5.15	5.07	10.1	—	2.92
11	<i>m</i> -Fluorosulfonyl-	3.80	3.51	8.5	—	2.64
12	<i>p</i> -Fluorosulfonyl-	6.05	6.34	11.5	—	4.54
<i>Acaricides</i>						
13	Ovex	8.04	4.18	10.4	—	9.00
14	Genite	6.90	3.60	10.1	—	8.94
15	Tedion (<i>p</i> -Chlorophenyl 2,4,5-trichlorophenylsulfone)	31.70	10.22	16.1	—	13.62

^a Underlined values indicate major peak. Bracket values indicate trace quantities.

^b Gas chromatographic parameters described in Table IV.

of these, experimental conditions and retention times are presented in Tables IV and V, respectively.

Fig. 1 illustrates the separation of the components of the isomeric chlorophenyl fluorosulfonyl-benzenesulfonates, fluorosulfonyl-benzenesulfonyl chlorides and acaricides on 5% OV-17 at 225°. Fig. 2 illustrates the separation of the components of the isomeric chlorophenyl *m*- and *p*-fluorosulfonyl-benzenesulfonates on 3% SE-30 at 200°. The numbering of the peaks corresponds to that in Table V. The use of a 5% OV-17 column at 225° (determination A, Tables IV and V) permitted the largest separation of isomeric constituents as well as the acaricides. However, this column does not separate the isomeric pairs 4 and 5 as well as 7 and 8 (e.g., *o*- and *m*-chlorophenyl sulfonate isomers of the chlorophenyl *m*- and *p*-fluorosulfonyl-benzenesulfonates, respectively). However, the above classes of isomers were separated on 3% SE-30 at 200°. A 10 ft. × ¼ in. O.D. 10% OV-1 column at 200° (determination C, Tables IV and V) was less effective in resolving the various isomeric components while the use of a spiral glass 6 ft. × ¼ in. O.D. column coated with 4.9% OV-17 at 240° (determination D) effected poor separation (with some concomitant degradation) of the various isomers of the chlorophenyl fluorosulfonyl-benzenesulfonates.

The order of retention of both the isomeric chlorophenyl fluorosulfonyl-benzenesulfonates and fluorosulfonyl-benzenesulfonyl chlorides on the non-polar SE-30, OV-1 and OV-17 liquid phases was $p > o > m$.

The use of an electron-capture detector (⁶³Ni) permitted an enhanced sensitivity compared to flame ionization for the detection of the isomeric chlorophenyl fluorosulfonyl-benzenesulfonates (e.g., 0.2–0.5 ng versus 1–3 ng for the latter). The response of these isomers compared to *p,p'*-DDT was 0.5 on a weight basis.

Attempts to achieve adequate separation of the variety of derivatives utilizing 3% OV-1 with temperature programming were generally unrewarding (Tables IV and V). It is also of interest to note that the retention times of the isomeric fluorosulfonyl-benzenesulfonyl chlorides were 2.9, 2.6 and 4.5 min for the *ortho*, *meta* and *para* isomers, respectively, versus 5.3, 5.3 and 7.7 min for their hydrolysis products (the respective isomeric fluorosulfonyl-benzenesulfonic acids, as determined by temperature programming determination E, Table IV).

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