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Note

Thin-layer and gas chromatographic separation of ferrocene oxathiolanes and dithiolanes

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Ferrocene derivatives are relatively stable organometallic compounds and have been analysed by means of thin-layer (TLC)^{1–3}, gas-liquid (GLC)^{4,5} and high-performance liquid chromatography (HPLC)^{6–8}. Some methods for the separation of ferrocene compounds from reaction mixtures have been proposed^{1,2,6,8}.

We have been investigating the application of chromatographic methods to the separation of oxygen- and sulphur-containing ferrocene derivatives³. In this paper we discuss the separation of selected ferrocene oxathiolanes and dithiolanes by means of TLC and GLC.

EXPERIMENTAL

Preparation of ferrocene compounds

Series of ferrocenyl dioxolanes, oxathiolanes and dithiolanes (see Table I) were prepared by reaction of formylferrocene and ferrocene ketones with 1,2-diols, 2-mercaptoethanol and 1,2-dimercaptoethane⁹. All of the derivatives were purified by column liquid chromatography. The glass column (40 × 3 cm I.D.) was filled with silica gel 60 (70–230 mesh) (E. Merck, Darmstadt, G.F.R.). The mobile phase was *n*-hexane-acetone (9:1).

Partition thin-layer chromatography

The sample substances were separated using pre-coated glass TLC plates covered with silanized silica gel 60-F₂₅₄ (E. Merck) and impregnated with 20% triethylene glycol in acetone. On these plates, 2 μl of a solution of the ferrocene derivatives in chloroform (5 mg/ml) were developed using *n*-hexane-carbon tetrachloride-benzene (12:1:1) as the mobile phase. The chromatograms were examined under UV light (254 nm).

Gas-liquid chromatography

A Perkin-Elmer 900 chromatograph with a flame-ionization detector was used, equipped with a glass column (6 ft. × 3 mm I.D.). The stationary phase was 3%

EGSP-Z on Gas-Chrom Q (100–120 mesh) (Applied Science Labs., State College, PA, U.S.A.). The operating conditions were as follows: detector temperature, 220°C; injection chamber temperature, 260°C; hydrogen flow-rate, 35 ml/min; air flow-rate, 180 ml/min; argon flow-rate, 40 ml/min. Isothermal analysis was performed at 220°C.

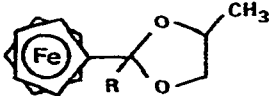

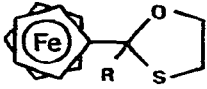
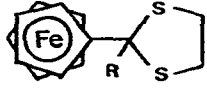
RESULTS AND DISCUSSION

Results of the partition TLC separation of the ferrocene derivatives are given as R_F values in Table I. The conditions used (non-reversed phase) gave more satisfactory separations than adsorption TLC.

The results show that substitution of oxathiolane or dithiolane rings with methyl or phenyl groups in the 2-position increases the R_F values.

The qualitative separation achieved by TLC was confirmed by the results obtained by GLC. The results of isothermal separation on EGSP-Z as the stationary phase are given in Fig. 1 and Table II. The separations obtained are also given in the

TABLE I
CHEMICAL CONSTITUTION AND R_F VALUES OF FERROCENE COMPOUNDS

Compound	Structural formula		R_F value
	Formula	R	
<i>Dioxolane:</i>			
2-Ferrocenyl-4-methyldioxolane-1,3		H	0.28
<i>Bisdithiolanes:</i>			
1,1'-Ferrocene-bis(dithiolane-1,3)		H	0.47
1,1'-Ferrocene-bis(2-methyldithiolane-1,3)		CH ₃	0.53
1,1'-Ferrocene-bis(2-phenyldithiolane-1,3)		C ₆ H ₅	0.58
<i>Oxathiolanes:</i>			
2-Ferrocenyloxathiolane-1,3		H	0.56
2-Ferrocenyl-2-methyloxathiolane-1,3		CH ₃	0.61
2-Ferrocenyl-2-phenyloxathiolane-1,3		C ₆ H ₅	0.67
<i>Dithiolanes:</i>			
2-Ferrocenyldithiolane-1,3		H	0.60
2-Ferrocenyl-2-methyldithiolane-1,3		CH ₃	0.65
2-Ferrocenyl-2-phenyldithiolane-1,3		C ₆ H ₅	0.71

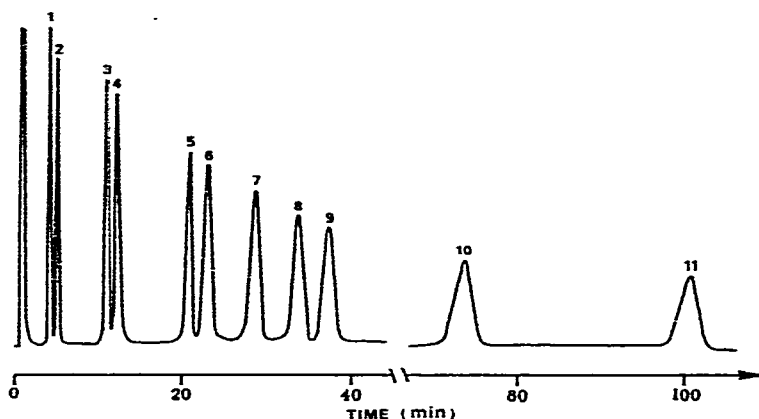


Fig. 1. Separation of a mixture of ferrocene oxathiolanes and dithiolanes using a 3% EGSP-Z column. Peaks: 1 = 2-ferrocenyl-4-methyldioxolane-1,3; 2 = internal standard (1,3-diphenylacetone); 3 = 2-ferrocenyloxathiolane-1,3; 4 = 2-ferrocenyl-2-methyloxathiolane-1,3; 5 = 2-ferrocenyldithiolane-1,3; 6 = 2-ferrocenyl-2-methyldithiolane-1,3; 7 = 2-ferrocenyl-2-phenyloxathiolane-1,3; 8 = 1,1'-ferrocene-bis(dithiolane-1,3); 9 = 1,1'-ferrocene-bis(2-methyldithiolane-1,3); 10 = 2-ferrocenyl-2-phenyldithiolane-1,3; 11 = 1,1'-ferrocene-bis(2-phenyldithiolane-1,3).

TABLE II

GLC RETENTION VALUES OF FERROCENE DERIVATIVES

Compound separated	Retention value	
	t_R (min)	α
<i>Internal standard:</i>		
1,3-Diphenylacetone	4.8	1.00
<i>Dioxolane-1,3:</i>		
2-Ferrocenyl-4-methyldioxolane-1,3	4.0	0.84
<i>Bisdithiolanes:</i>		
1,1'-Ferrocene-bis(dithiolane-1,3)	33.5	7.05
1,1'-Ferrocene-bis(2-methyldithiolane-1,3)	37.0	7.78
1,1'-Ferrocene-bis(2-phenyldithiolane-1,3)	102.0	21.05
<i>Oxathiolanes:</i>		
2-Ferrocenyloxathiolane-1,3	10.5	2.21
2-Ferrocenyl-2-methyloxathiolane-1,3	12.0	2.52
2-Ferrocenyl-2-phenyloxathiolane-1,3	28.5	6.00
<i>Dithiolanes:</i>		
2-Ferrocenyldithiolane-1,3	20.5	4.31
2-Ferrocenyl-2-methyldithiolane-1,3	22.8	4.78
2-Ferrocenyl-2-phenyldithiolane-1,3	74.8	15.58

form of retention times (t_R) and relative retention times (α), determined relative to the retention time of the internal standard, 1,3-diphenylacetone.

Application of the polar stationary phase EGSP-Z (McReynolds constant $\Sigma AI = 2278$) permits the isothermal separation of the sample substances. Silicone stationary phases of the OV or SE type did not give efficient separations.

REFERENCES

- 1 K. Schlögl and H. Egger, *Monatsh. Chem.*, 94 (1963) 376.
- 2 R. E. Bozak and J. H. Fukuda, *J. Chromatogr.*, 26 (1967) 501.
- 3 L. Ogierman, B. Czech and A. Piórko, *J. Chromatogr.*, 198 (1980) 536.
- 4 O. E. Ayers, T. G. Smith, J. D. Burnett and B. W. Ponder, *Anal. Chem.*, 38 (1966) 1606.
- 5 C. Pomier and G. Guiochon, *Chromatographia*, 2 (1969) 346.
- 6 M. Shiga, M. Tsunashima, H. Kono, J. Motoyama and K. Hata, *Bull. Chem. Soc. Jap.*, 43 (1970) 841.
- 7 D. T. Haworth and T. Liu, *J. Chromatogr. Sci.*, 14 (1976) 519.
- 8 M. T. McKone, *J. Chem. Educ.*, 57 (1980) 380.
- 9 A. Ratajczak and B. Czech, *Rocz. Chem.*, 51 (1977) 1735.