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Note

Gas chromatographic separation of some dihalobenzene isomers and some substituted monohalobenzene isomers

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There are many reports in the literature on the gas chromatographic (GC) separation of dihalobenzene isomers¹⁻¹³. The ten possible sets of dihalobenzene isomers have all been separated by GC. However, in most cases the retention times, in particular the retention time for the appropriate *ortho* isomer (always the last isomer to come off the column), were inconveniently long and the resolution obtained between the *meta* and *para* isomers was not always 100%^{3,7}. Since we wished, in connection with another project, to separate rapidly and with high resolution on the same column some of the dihalobenzene isomers and some substituted monohalobenzene isomers, we experimented with a number of stationary phases and used seven sets of dihalobenzene isomers. This paper describes how a number of stationary phases on Chromosorb W were tried. The most successful stationary phase was a mixture of bentone 34 (10%) and dinonylphthalate (DNP) (5%). With this stationary phase not only could a virtual 100% resolution be achieved in the separation of the respective *ortho*, *meta* and *para* isomers but, in almost all cases, a dramatic improvement in the retention times, particularly of the *ortho* isomer, was achieved.

EXPERIMENTAL

Chemicals

The sets of isomers used were obtained from Aldrich, Milwaukee, WI, U.S.A. (fluorobromo-, dichloro- and chlorocycano benzenes and bromoanisoles), Koch-Light, Colnbrook, Great Britain (fluorochloro-, dibromo-, difluoro- and fluoriodo benzenes) and Mersey Chem., Liverpool, Great Britain (bromochlorobenzenes). All other chemicals used were normal laboratory grade and were used without further purification.

Gas chromatograph and columns

Chromatographic measurements were made on a Pye-Unicam series 105 gas chromatograph with a flame ionization detector, and this was linked to an Infotronic CRS 309 integrator for exact retention time data. The samples injected were 1 μ l in all cases. The mixtures for testing were prepared by mixing equal weights (20 mg) of each pure isomer and the appropriate monohalo hydrocarbon in benzene (1 ml).

The most successful column (that containing 10% bentone and 5% DNP) was prepared as follows: Chromosorb W, 100-200 mesh (8 g) was mixed with bentone 34

(0.8 g) and DNP (0.4 g) in dichloromethane. The solvent was (roto) vaporated off under reduced pressure and the remaining solid material was used to pack the column, which was conditioned overnight at 200°C prior to use. The 10% bentone-10% DNP, 10% bentone-20% DNP, 5% bentone-5% DNP and 10% bentone columns were similarly prepared.

RESULTS AND DISCUSSION

The results of our work with nine sets of isomers are shown in Table I. The best separations and shortest retention times for the *ortho* isomers were obtained with 10% bentone-5% DNP and the chromatographs obtained are shown in Figs. 1 and 2. The baseline separations of the isomers with 100% resolution are evident in all cases. In many cases the parent monohalohydrocarbon separates out also though in the case of the dichloro compound chlorobenzene is not properly resolved from *p*-dichlorobenzene and for the conditions used for the difluorobenzene isomers, fluorobenzene had the same retention time as benzene.

TABLE I

RETENTION TIMES OF DIHALO- AND SUBSTITUTED MONOHALOBENZENES

Conditions: 1.5 m × 4 mm I.D. glass column with stationary phase(s), as shown on Chromosorb W, 100-200 mesh. Oven temperature, 155°C unless indicated. Nitrogen carrier flow-rate 100 ml/min.

Compound	Retention time (min)								
	10% Bentone			10% Bentone-5% DNP			10% Bentone-10% DNP		
	<i>p</i> -	<i>m</i> -	<i>o</i> -	<i>p</i> -	<i>m</i> -	<i>o</i> -	<i>p</i> -	<i>m</i> -	<i>o</i> -
Bromochloro-	4.4	8.4	14.5	2.3	3.8	7.6*	5.2	6.2	9.7
Dibromo-	7.4	15.0	26.2	3.5	6.1	12.4	8.3	10.1	15.7
Dichloro-	2.4	4.3	8.5	1.6	2.7	5.5*	3.1	3.6	5.7
Bromomethoxy-	26.6	29.4	50.2*	16.6	19.3	33.8*	16.3	17.8	27.6
Fluorochloro-	1.3	1.8	3.1	0.8	1.2	2.0	1.3	1.4	2.1
Fluorobromo-	1.8	2.8	5.1	1.1	1.6	3.0	2.0	2.2	3.3
Fluoriodo-	3.1	4.9	9.3	2.0	2.9	5.5	3.6	4.0	6.1
Difluoro-	1.2	1.6	2.8**	0.9	1.3	3.0***	0.8	0.8	1.8
Chlorocyno-	11.6	14.8	34.1	4.9	10.2	24.6	9.4	12.6	29.2

* Temperature 165°C.

** Temperature 110°C.

*** Temperature 90°C.

With 10% bentone as the stationary phase (see Table I) the compounds with large groups have difficulty in being eluted. This *o*-bromoanisole is not eluted until *ca.* 50 min, even at 165°C. However, this column is very good for those compounds having smaller substituents and, for example, an excellent separation of difluorobenzenes is obtained at 110°C.

In the 10% bentone-10% DNP column the effect of the widening of the pores of the bentone by the DNP is obvious in, for example, the shorter retention time of *o*-bromoanisole. However, poor resolution of the *para* and *meta* isomers is obtained in this case.

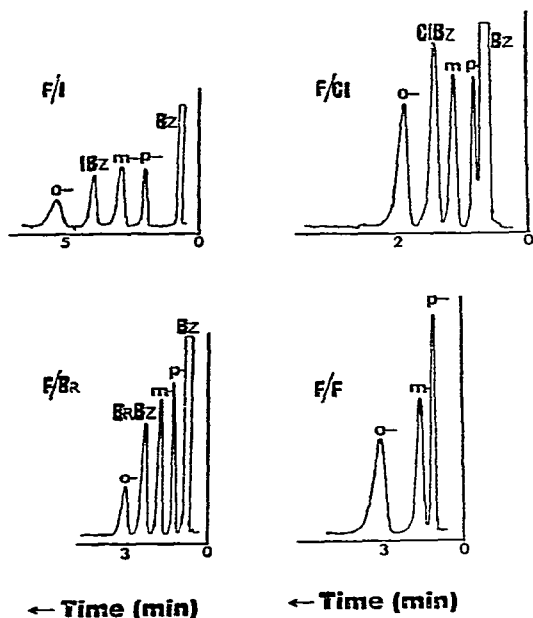


Fig. 1. Chromatograms for the separation of monohalo-fluorobenzenes. F/I, iodofluoro; F/Cl, chlorofluoro; F/Br, bromofluoro; F/F, difluoro; IBz, iodobenzene; ClBz, chlorobenzene; FBz, fluorobenzene; Bz, benzene. See Table I for conditions. In the separation of the difluorobenzenes, Bz and FBz have the same retention times as *m*-difluorobenzene.

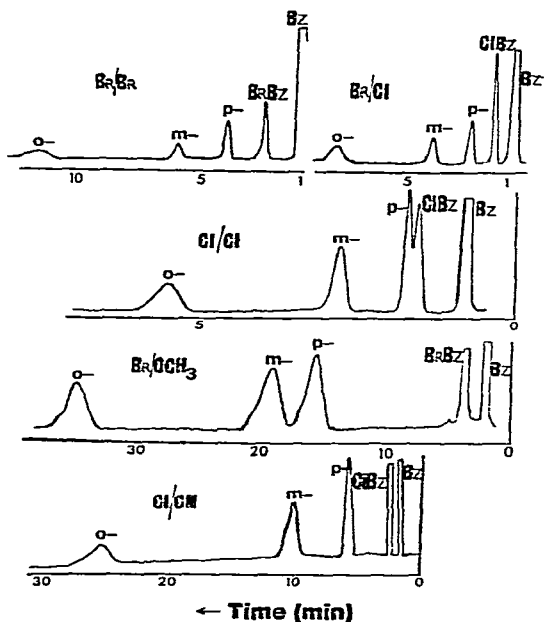


Fig. 2. Chromatograms for the separation of various bromo- and chloro-benzenes. Br/Br, dibromo; Br/Cl, bromochloro; Cl/Cl, dichloro; Br/OCH₃, bromomethoxy; Cl/CN, chlorocyno; BrBz, bromobenzene; ClBz, chlorobenzene; Bz, benzene. See Table I for conditions. In the separation of the bromochlorobenzenes, BrBz and *m*-bromochlorobenzene have the same retention times.

With 10% bentone–20% DNP separation of the *para* and *meta* isomers could not be achieved for any of the compounds studied. With 5% bentone–5% DNP the separation of *p*- and *m*-bromochlorobenzenes could not be done and these columns were not employed in any further studies.

In Table II our retention times using the 10% bentone–5% dinonylphthalate as a stationary phase are compared with the available literature values. It is seen that in all cases (except for the dibromo/dichlorobenzenes) the time taken to achieve a

TABLE II
COMPARISON OF RETENTION TIMES FOR DIHALO- AND SUBSTITUTED MONOHALO-BENZENES

Compound	Retention time (min)			Ref.
	<i>p</i> -	<i>m</i> -	<i>o</i> -	
Bromochloro-	19.4	17.9	24.1	7
	4.2	7.0	13.2	8
	6.64	8.7	14.2	11
	2.3	3.8	7.6	This work
Dibromo-	<i>ca.</i> 4.5*	<i>ca.</i> 7.0*	<i>ca.</i> 13.0*	2
	2.7	3.3	4.7	6
	26.4	24.7	32.9	7
	11.5	15.6	25.5	11
	3.5	6.1	12.4	This work
Dichloro-	<i>ca.</i> 10.0	<i>ca.</i> 22.0	<i>ca.</i> 57.0	1
	<i>ca.</i> 20.5	<i>ca.</i> 17.0	<i>ca.</i> 26.0	3
	13.5	12.2	16.6	7
	3.0	3.5	4.9	9
	7.74	10.3	17.9	11
	—**	—**	13.0	13
	1.6	2.7	5.5	This work
Bromomethoxy-	46.6	52.8	63.0	4
	16.6	19.3	33.8	This work
Fluorochloro-	32.1	25.1	37.9	7
	1.71	2.3	3.85	10
	4.41	5.62	9.65	11
	0.8	1.2	2.0	This work
Fluorobromo-	<i>ca.</i> 22.0	<i>ca.</i> 18.0	<i>ca.</i> 26.0	5
	13.5	11.5	16.2	7
	5.59	7.2	12.4	11
	1.1	1.6	3.0	This work
Fluoroiodo-	18.3	16.6	23.0	7
	6.92	8.77	14.4	11
	2.0	2.9	5.5	This work
Difluoro-	16.8	12.9	17.6	7
	4.9	5.83	9.8	11
	0.9	1.3	3.0	This work
Chlorocyano-	6.9	10.2	24.6	This work

* Estimated from drawing in paper referred to.

** Not determined.

complete separation of isomers has been approximately halved and in some cases reduced by a factor of three or four.

It is thus evident that not only is the column efficient for fast elution with good resolution and separation but it is also quite versatile. The columns packed by us were not, however, suitable for the separation of the bromotoluene or bromonitrobenzene isomers.

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REFERENCES

- 1 C. T. Cowan and J. M. Hartwell, *Nature (London)*, 190 (1961) 712.
- 2 E. V. Kolbasina and N. I. Lulova, *Zavod. Labor.*, 35 (1969) 1444.
- 3 A. E. Habboush and A. H. Tameesh, *J. Chromatogr.*, 53 (1970) 143.
- 4 A. E. Habboush and A. H. Tameesh, *J. Chromatogr.*, 53 (1970) 151.
- 5 A. E. Habboush and A. H. Tameesh, *J. Chromatogr.*, 54 (1971) 145.
- 6 F. W. Karasek, *J. Chromatogr. Sci.*, 8 (1970) 282.
- 7 L. Vasaros, H. J. Machulla and W. Tornau, *J. Chromatogr.*, 62 (1971) 458.
- 8 F. W. Karasek and P. Vassilakopoulos, *Chromatographia*, 4 (1971) 388.
- 9 F. W. Karasek and I. Fong, *J. Chromatogr. Sci.*, 9 (1971) 497.
- 10 F. W. Karasek, A. I. Grimard and B. L. Deelstra, *J. Chromatogr. Sci.*, 10 (1972) 725.
- 11 E. J. Knust and M. Schüller, *J. Chromatogr.*, 114 (1975) 207.
- 12 A. E. Habboush and K. A. B. Najm, *J. Chromatogr.*, 130 (1977) 161.
- 13 Z. Witkiewicz and S. Popiel, *J. Chromatogr.*, 154 (1978) 60.