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Note

Gas chromatographic separation of mono- and disubstituted benzene derivatives and of diastereoisomeric halogenoalkanes with Bentone-38

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The halogenation of benzene and its monosubstituted derivatives gives rise to a mixture of the unchanged substrate, the mono-halogenated compound and its halogenated *ortho*-, *meta*- and *para*-isomers. In the course of our studies on electrophilic and hot homolytic substitution reactions by nucleogenic recoil atoms, the halogenated derivatives are formed in carrier-free amounts labelled with the respective radioactive halogen atom[1–5]. The label was a short-lived radiohalogen such as ^{18}F ($t_{\frac{1}{2}}$ = 110 min), ^{38}Cl ($t_{\frac{1}{2}}$ = 37 min) and ^{80}Br ($t_{\frac{1}{2}}$ = 18 min). Therefore, a fast separation method had to be developed in order to allow radioactivity measurements with a reasonable statistical error. Gas–liquid chromatographic (GLC) techniques provide rapid analytical methods for the separation of compounds having similar boiling points. Besides fast separation, a good resolution of the peaks is also desirable. In our experimental work, the halogenated products were injected into the column in the presence of large quantities of the unchanged substrate and a solvent (carbon tetrachloride). The total volume of the reaction mixture was $\leqslant 400\,\mu l$, which could not be separated with capillary columns.

In the literature, separations of isomeric substituted benzenes by GLC techniques are described[6–14] and our laboratory has recently reported[6] a fast method for the separation of disubstituted benzenes and diastereoisomeric halogenolkanes using Igepal CO-880 on a stationary phase. In some of the papers[11–15] the application of solid Bentone-34 (dimethyldioctadecylammonium bentonite) in a mixture with liquid silicone oil or dinonyl phthalate is mentioned as an appropriate stationary phase for the separation of such aromatic compounds. Mortimer and Gent[11] suggested from X-ray studies that the selectivity found for the various isomers is based on the expansion of the basal spacing of the organoclay in Bentone from 12.3 to 38.5 Å caused by the silicone oil, the Bentone thus being present as a thixotropic gel. Most of these studies, however, had the disadvantages of long retention times, incomplete separations or the necessity of small sample sizes[14–16]. Similar problems occur in GLC separations of diastereoisomeric halogenoalkanes. The liquid phases used so far, *e.g.*, Carbowax 20 M[17], Carbowax 300[18] or tritolyl phosphate[19], did not yield satisfactory results with regard to retention time and/or resolution.

When looking for a versatile column, combining the advantages of rapid separation and good resolution, we found Bentone-38 to be a good material for our analyt-

TABLE I

DATA FOR GLC SEPARATION OF *o*-, *m*-, *p*-ISOMERS AND THE MONOSUBSTITUTED BENZENE COMPOUNDS WITH BENTONE-38

Column (glass, 3.5 mm I.D.) filled with 6% Bentone-38 and 20% silicone oil DC 200 on Chromosorb W-AW-DMCS (60–80 mesh). t_{net} = absolute retention time; r = relative retention time.

Y	*X*	C_6H_5Y		C_6H_5X		*ortho*		*meta*		*para*		*Dodecane standard*		*Temp. (°C)*	*Inlet pressure (kg/cm²)*
		t_{net} (min)	r	t_{net} (min)	r	t_{net} (min)	r	t_{net} (min)	r	t_{net} (min)	r	t_{net} (min)	r		
F	F	6.88	1.180			9.81	1.683	5.83	1.000	4.89	0.839			70	2.32
	Cl	2.01	0.358	7.24	1.288	9.65	1.717	5.62	1.000	4.41	0.785	33.07	5.884	110	2.60
	Br	1.57	0.218	9.52	1.320	12.39	1.718	7.21	1.000	5.59	0.775	21.94	3.043	120	2.67
	I	1.12	0.128	11.31	1.290	14.35	1.636	8.77	1.000	6.92	0.789	12.98	1.480	140	2.79
Cl	Cl	4.47	0.433			17.89	1.734	10.32	1.000	7.74	0.750	17.77	1.722	130	2.73
	Br	2.56	0.294	4.27	0.490	14.15	1.623	8.72	1.000	6.64	0.761	8.27	0.948	150	2.85
	I	2.56	0.147	8.04	0.461	28.09	1.610	17.45	1.000	13.08	0.750	8.27	0.474	150	2.85
	CF_3	7.24	1.240	2.71	0.464	14.75	2.526	5.84	1.000	4.31	0.738	33.07	5.663	110	2.60
	NO_2	1.38	0.101	7.32	0.537	26.92	1.975	13.63	1.000	8.41	0.617	3.61	0.265	180	3.03
Br	Br	4.27	0.274			25.51	1.638	15.57	1.000	11.47	0.737	8.27	0.531	150	2.85
	I	3.70	0.157	6.65	0.282	37.45	1.588	23.58	1.000	17.17	0.728	7.36	0.312	160	2.91
	CF_3	7.91	1.280	1.76	0.285	14.42	2.333	6.18	1.000	4.56	0.738	17.77	2.875	130	2.73
	CN	2.27	0.149	4.33	0.284	33.52	2.195	15.27	1.000	9.37	0.614	3.61	0.236	180	3.03
I	I	3.52	0.182			28.69	1.484	19.33	1.000	14.55	0.753	3.61	0.187	180	3.03
	CF_3	11.31	1.285	1.40	0.159	19.00	2.159	8.80	1.000	6.73	0.765	12.98	1.475	140	2.79

ical problems, also being useful on a semi-preparative scale. Here we report the application of Bentone-38–silicone oil DC 200 as a phase for the separation of both mono- and disubstituted aromatic compounds and diastereoisomeric halogenoalkanes. The results of these investigations are summarized and compared with previous separations described in the literature.

EXPERIMENTAL

All GLC analyses were performed with a Hewlett-Packard Research Chromatograph 5752, using a thermal-conductivity detector. The columns used (glass; length 4 m, 3.5 mm I.D.) were filled with 6% Bentone-38 (highly purified montmorillonite, Al_2O_3–$4SiO_2$–H_2O + nH_2O, dried at 150° to give $Al_2(OH)_2(SiO_{10})$ and then treated with dimethyldioctadecylammonium chloride) and 20% silicone oil DC 200 on Chromosorb W-AW-DMCS (60–80 mesh). Bentone-38 and silicone oil DC 200 were obtained from E. Merck, Darmstadt, G.F.R. The material was prepared by mixing the compounds with the solid support in dichloromethane and then removing the solvent by the rotating-evaporator method.

The experimental data in Tables I and II were obtained after injecting a mixture of the isomeric compounds and the standard (*ca.* 0.2 μl of each compound). Because of larger amounts of the unchanged substrate and the solvent (carbon tetrachloride), the actual temperature conditions of analysis had to be varied and therefore differ somewhat from the given data. In all cases, helium was used as carrier gas with a flow-rate of 100 ml/min.

RESULTS AND DISCUSSION

The results of the separation of the *ortho*-, *meta*- and *para*-isomers of fluoro-, chloro-, bromo- and iodobenzenes are shown in Table I together with data for the monosubstituted compounds. The retention times are given on an absolute scale (min) and relative to an internal standard (*meta*-isomer, relative retention time = 1). Also, an aliphatic substrate (dodecane) was added as a standard compound. All the separations could be performed in less than 38 min, less than the hitherto shortest retention times of a similar analysis using Igepal CO-880 on Chromosorb W-AW-DMCS[6]. In all cases, the resolution was 100%. The tailing peaks in the case of *ortho*-chloronitrobenzene and *ortho*-bromobenzonitrile were possibly due to partial decomposition of the compounds; in this case the retention times were determined from the minimum amounts (*ca.* 0.02 μl) of the isomers.

Bentone-38 is also well suited for the separation of diastereoisomeric halogenoalkanes. Analysis data for 1,2-dichloro-1,2-difluoroethane, 2-bromo-3-fluorobutane, 2,3-dichlorobutane, 2-bromo-3-chlorobutane and 2,3-dibromobutane are summarized in Table II, showing absolute and relative retention times (*racemic*- and *threo*-compound, relative retention time = 1). In all cases, decane was present as an internal standard. In contrast to separations with other columns described[4,18,19] the analysis of all the diastereoisomeric compounds can be performed in less than 5 min and has a resolution of 100%. Especially in the difficult case of 1,2-dichloro-1,2-difluorethane (b.p. 59.4 and 59.9°, respectively), an excellent separation can be achieved within 5 min.

TABLE II

DATA FOR GLC SEPARATION OF DIASTEREOISOMERIC 1,2-DICHLORO-1,2-DIFLUOROETHANES AND 2,3-HALOGENOBUTANES

Column as in Table I.

Compound	*meso or erythro*		*racemic or threo*		*Decane standard*		*Temp. (°C)*	*Inlet pressure (kg/cm²)*
	t_{net} *(min)*	*r*	t_{net} *(min)*	*r*	t_{net} *(min)*	*r*		
1,2-Dichloro-1,2-difluoroethane	3.99	0.819	4.87	1.000			50	2.17
2-Bromo-3-fluorobutane	2.08	0.614	3.39	1.000	7.95	2.345	120	2.67
2,3-Dichlorobutane	2.34	0.692	3.38	1.000	5.93	1.754	130	2.73
2-Bromo-3-chlorobutane	2.90	0.749	3.87	1.000	4.45	1.150	140	2.79
2,3-Dibromobutane	3.05	0.784	3.89	1.000	2.85	0.733	160	2.91

In conclusion, for separation of mono- and disubstituted halogenobenzenes and diastereoisomeric halogenoalkanes, Bentone-38 (with silicone oil DC 200) on Chromosorb W-AW-DMCS is an efficient material with short retention times and very good resolution properties. The only disadvantage is the maximum temperature (180°), usage being limited to lower boiling substances (boiling points less than *ca.* 250°).

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