

## Notes

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### Gas chromatography of isomeric pentyl halides

Research currently in progress in these laboratories is concerned with alkyl rearrangements which may occur during the interactions of the eight isomeric pentyl alcohols with halogenating agents. A number of such rearrangements have been known for a long time and were first recognised by means of refractive index measurements and tests of hydrolytic stability. Secondary alcohols and those branched at the  $\beta$ -carbon atom are particularly prone to rearrangement<sup>1</sup>. Whilst it seems unlikely that in the reaction of any one alcohol all possible isomeric halogenopentanes would be obtained, it is nevertheless important to be able to show with certainty the presence or absence of any particular isomer in a reaction product. A method has therefore been devised for the analysis of such mixtures by gas chromatography. Separations have previously been reported only for the straight chain (1-, 2- and 3-)halogenopentanes<sup>2-4</sup>.

#### Experimental

*Materials.* 1-Halogenopentanes were obtained commercially and redistilled.

Isomerically pure 2- and 3-halogenopentanes were prepared as described previously, by the use of phosphorus trihalides under specified conditions<sup>5</sup>.

The branched chain halogenomethylbutanes were prepared from the corresponding alcohols (Table I), as described previously for the straight chain isomers<sup>5</sup>, and purified if necessary by preparative gas chromatography.

Neopentyl halides (1-halogeno-2,2-dimethylpropanes): The chloride was obtained by thermal decomposition of neopentyl chlorosulphite (100°/100 h), in the presence of pyridine hydrochloride (0.01 mol.)<sup>6</sup>. The primary product (52 % yield) contained both neo- (58 %) and *tert.*- (42 %) pentyl chlorides and was shaken vigorously with an equal volume of 2 *N* nitric acid to remove the *tert.*-isomer. Periodic examination by GLC during this process showed hydrolysis to be slow; about 12 h were necessary for equilibration of the system:  $\text{tert.}-\text{PeCl} + \text{H}_2\text{O} \rightleftharpoons \text{tert.}-\text{PeOH} + \text{HCl}$ . *tert.*-Pentyl alcohol was then removed by aqueous washing and the whole process repeated eight times to achieve complete purification.

Isomerically pure neopentyl bromide and iodide were prepared by described methods, by interaction of neopentyl alcohol with triphenylphosphine dibromide<sup>7</sup> and triphenyl phosphite-methiodide<sup>8,9</sup> respectively.

The identities of all halides were confirmed by halogen analysis and n.m.r. examination. Infrared absorption frequencies were recorded in the KBr region for the purpose of assisting in the characterization of mixtures.

*Apparatus.* Purifications by preparative scale GLC were carried out with a 4 ft.  $\times$  3/4 in. O.D. glass column packed with squalane (15 %) on 85-100 mesh Celite. A temperature of 50° and nitrogen flow-rate of 250-300 ml/min were employed.

Analytical separations were mostly performed on a Perkin-Elmer F. 11 chromatograph with nitrogen carrier gas and flame ionization detector. Two columns were used:

TABLE I

## PREPARATION OF HALOGENOMETHYLBUTANES

Alcohol (ROH)	Reagent (mol.)		Reaction		Yield <sup>a</sup> (mol.)	Alkyl halide composition (%) <sup>b</sup>			
	g. (1 mol)		Temp. (°C)	Time		Me <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> X	EtMeCHCH <sub>2</sub> X	Me <sub>2</sub> CHCHXMe	Me <sub>2</sub> EtCX
Me <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub>	16.74	PCl <sub>3</sub> (0.37)	-10	15 min	0.16	100	—	—	—
	8.23	PBr <sub>3</sub> (0.37)	-10	15 min	0.17	100	—	—	—
	5.50	PI <sub>3</sub> (1.00)	20	60 h	0.32	100	—	—	—
EtMe <sub>2</sub> CHCH <sub>2</sub>	44.95	PCl <sub>3</sub> (0.33)	-15	15 min	0.17	—	99	—	1 <sup>c</sup>
	32.60	PBr <sub>3</sub> (0.37)	-10	15 min	0.24	—	100	—	—
	11.00	PI <sub>3</sub> (1.00)	20	48 h	0.40	—	100	—	—
Me <sub>2</sub> CHCHMe	35.54	PCl <sub>3</sub> (0.33)	-15	15 min	0.24	—	—	14	86 <sup>d</sup>
	30.75	PBr <sub>3</sub> (1.00)	-15	15 min	0.70	—	—	20	80 <sup>d</sup>
	11.00	PI <sub>3</sub> (1.00)	20	48 h	0.49	—	—	24	76 <sup>d</sup>
Me <sub>2</sub> EtCe	30.10	HCl (2.00) <sup>f</sup>	20	15 min	0.63	—	—	—	100
	32.40	HBr (2.00) <sup>f</sup>	20	15 min	0.43	—	—	—	100
	10.00	HI (2.00) <sup>f</sup>	20	15 min	0.25	—	—	—	100

<sup>a</sup> Distilled product. Crude reaction products were washed and dried before distillation.

<sup>b</sup> Skeletal rearrangements (*i.e.* involving methyl shifts) were not observed.

<sup>c</sup> *tert.*-Isomer removed by prolonged washing with 2*N* HNO<sub>3</sub>.

<sup>d</sup> Isomers separated by preparative GLC.

<sup>e</sup> *tert.*-Pentyl.

<sup>f</sup> Concentrated aqueous acid.

TABLE II  
RELATIVE RETENTION TIMES AND CHARACTERIZATION DATA FOR PENTYL HALIDES

Compound	Relative retention times		B.p. (°C)	$n_D^{20}$	Infrared $\nu_{\max}$ ( $\text{cm}^{-1}$ ) <sup>a</sup>		
	Squalane	Bentone					
1-Chloro-2,2-dimethylpropane	1.00	1.00	83	1.4038	764(s)	722(s)	470(m)
2-Chloro-2-methylbutane	1.00	1.13	85	1.4049	778(m)	618(m)	561(s)
2-Chloro-3-methylbutane	1.37	1.47	93	1.4093	785(s)	673(s)	649(s)
2-Chloropentane	1.52	1.80	96	1.4052	759(s)	747(s)	671(s)
3-Chloropentane	1.63	1.86	97	1.4095	657(s)	634(m)	606(s)
1-Chloro-3-methylbutane	1.68	1.70	99	1.4070	727(s)	656(s)	
1-Chloro-2-methylbutane	1.83	1.83	100	1.4120	774(s)	730(s)	683(s)
1-Chloropentane	2.41	2.66	108	1.4120	731(s)	654(s)	
1-Bromo-2,2-dimethylpropane	1.00	1.00	105	1.4372	746(m)	656(s)	452(m)
2-Bromo-2-methylbutane	1.00	(1.15) <sup>b</sup>	63/165 mm	1.4416	799(s)	772(s)	510(s)
2-Bromo-3-methylbutane	1.33	1.52	115	1.4428	775(s)	617(s)	606(s)
2-Bromopentane	1.42	1.86	117	1.4380	756(s)	747(s)	617(s)
3-Bromopentane	1.55	1.93	117	1.4412	604(s)	531(s)	490(s)
1-Bromo-3-methylbutane	1.55	1.67	120	1.4410	752(m)	647(s)	565(s)
1-Bromo-2-methylbutane	1.68	1.82	120	1.4428	765(s)	650(s)	617(s)
1-Bromopentane	2.15	2.69	129	1.4443	732(s)	643(s)	564(s)
1-Iodo-2,2-dimethylpropane	1.00	1.00	40/25 mm	1.4886	742(m)	607(s)	447(m)
2-Iodo-2-methylbutane	0.97	(1.08) <sup>b</sup>	40/25 mm	1.4997	794(s)	763(s)	487(s)
2-Iodo-3-methylbutane	1.33	1.54	141	1.4993	771(s)	578(s)	423(m)
2-Iodopentane	1.39	1.77	145	1.4915	744(s)	580(s)	491(s)
3-Iodopentane	1.53	1.90	146	1.4982	798(s)	771(s)	574(s)
1-Iodo-3-methylbutane	1.53	1.58	147	1.4941	735(s)	594(s)	510(m)
1-Iodo-2-methylbutane	1.66	1.78	148	1.4972	794(m)	763(s)	602(s)
1-Iodopentane	2.14	2.51	155	1.4947	726(s)	592(s)	505(m)
							465(s)
							483(m) 460(m)
							582(s)

<sup>a</sup> KBr region. Weak absorptions not recorded.

<sup>b</sup> Determined in 1 m glass column at 20°.

(a) 4 m  $\times$  1/16 in. O.D. stainless steel column containing squalane (10%) on 80-100 mesh Chromosorb W. An inlet pressure of 30 p.s.i. gave a nitrogen flow-rate of 13-15 ml/min. Chlorides were analyzed at 20°; bromides and iodides at 40°.

(b) 4 m  $\times$  1/8 in. O.D. stainless steel column containing bentone 34 (11.5%) and silicone MS 555 (11.5%) on 80-100 Chromosorb W. A nitrogen flow-rate of 25-30 ml/min (inlet pressure 25 p.s.i.) and temperature of 40° were employed for all halides.

As *tert.*-pentyl bromide and iodide were unstable under the above conditions on column (b), mixtures containing these isomers were further examined in a 1 m  $\times$  1/4 in. O.D. glass column containing the same bentone-silicone stationary phase. For this a Pye Argon chromatograph was used, with argon flow-rate of 60 ml/min and column temperature of 20°.

Infrared spectra were recorded for liquid films on a Perkin-Elmer 137 KBr spectrometer.

### Results and discussion

Relative retention times for the conditions given above are shown in Table II, together with other characterization data determined for the pure isomers. The strongest infrared absorptions in the KBr region are included to assist in the identification of isomers in mixtures.

Typical chromatograms (for the chlorides) appear in Figs. 1 and 2. On squalane, the isomers eluted in order of increasing boiling point. The narrow bore squalane column afforded much greater efficiency than had been obtained in earlier work with

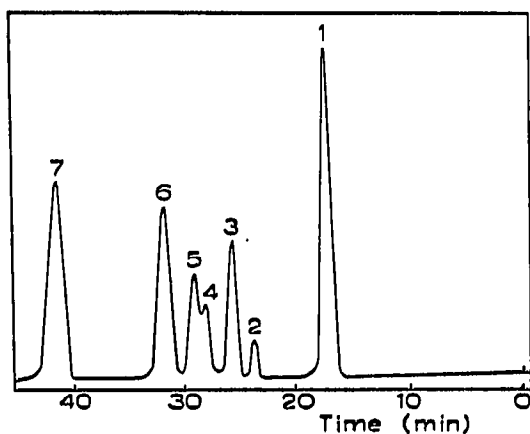


Fig. 1.

Fig. 1. Gas chromatogram of isomeric pentyl chlorides on squalane column. 1 = 1-chloro-2,2-dimethylpropane and 2-chloro-2-methylbutane; 2 = 2-chloro-3-methylbutane; 3 = 2-chloropentane; 4 = 3-chloropentane; 5 = 1-chloro-3-methylbutane; 6 = 1-chloro-2-methylbutane; 7 = 1-chloropentane.

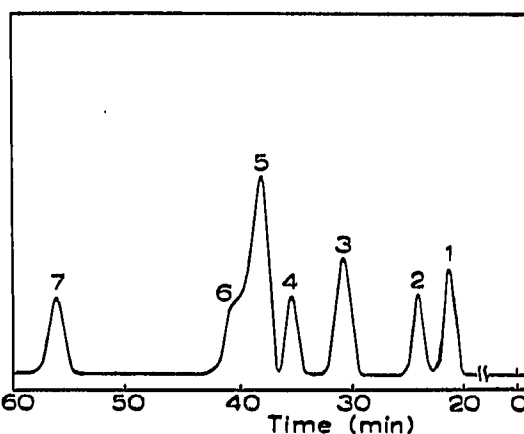


Fig. 2.

Fig. 2. Gas chromatogram of isomeric pentyl chlorides on modified bentone column. 1 = 1-chloro-2,2-dimethylpropane; 2 = 2-chloro-2-methylbutane; 3 = 2-chloro-3-methylbutane; 4 = 1-chloro-3-methylbutane; 5 = 1-chloro-2-methylbutane and 2-chloropentane; 6 = 3-chloropentane; 7 = 1-chloropentane.

the straight chain halides<sup>2</sup>, thus the complete resolution of 2- and 3-halogenopentanes was easily achieved. Two separations which were not possible on this column, *viz.* the 1-halogeno-2,2-dimethylpropanes (neopentyl halides) from the 2-halogeno-2-methylbutanes (*tert.*-pentyl halides), and the 3-halogenopentanes from the 1-halogeno-3-

methylbutanes, were achieved on a modified bentone column, a type which has hitherto been applied mainly to the separation of aromatic compounds and hydrocarbons<sup>10,11</sup>. Of a large number of other stationary phases investigated, none afforded separation of the first mentioned pair of isomers.

*tert.*-Pentyl bromide and iodide were unfortunately decomposed to a considerable extent in the 4 m bentone column, although not on squalane. This difficulty was overcome for the bromide by use of a short (1 m) glass column at 20°, in which good resolution from neopentyl bromide was obtained, without observable decomposition.

*tert.*-Pentyl iodide was still decomposed appreciably however, even under these conditions, and is best determined by aqueous hydrolysis or infrared analysis, after preparative scale separation of all except the neo- and *tert.*-isomers on squalane. Repeated use of the bentone column for these unstable halides resulted in loss of resolving power.

The 3-halogenopentanes were the only isomers which could not be completely separated from all other pentyl structures. This represents no disadvantage unless the 2- and 3-halogenopentanes, the 1-halogeno-2-methylbutanes and the 1-halogeno-3-methylbutanes, are all present in one sample, in which case the 3-halogenopentane content may be obtained by calculation from both chromatograms. Such a combination of products is unlikely to be obtained. With boron tribromide, a reagent which favours alkyl rearrangement, the straight chain pentanols gave only straight chain halides<sup>12</sup>; preliminary experiments with the branched pentyl alcohols indicate that in no case would all these isomers be produced.

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- 1 W. GERRARD AND H. R. HUDSON, *Chem. Rev.*, 65 (1965) 697.
- 2 W. GERRARD AND H. R. HUDSON, *J. Chem. Soc.*, (1963) 1059; *ibid.*, (1964) 2310.
- 3 H. J. WESSELMAN AND G. W. MILLS, *J. Gas Chromatog.*, (1964) 344.
- 4 J. CASON AND J. S. CORREIA, *J. Org. Chem.*, 26 (1961) 3645.
- 5 E. J. COULSON, W. GERRARD AND H. R. HUDSON, *J. Chem. Soc.*, (1965) 2364.
- 6 W. GERRARD AND P. TOLCHER, *J. Chem. Soc.*, (1954) 3640.
- 7 G. A. WILEY, R. L. HERSHKOWITZ, B. M. REIN AND B. C. CHUNG, *J. Am. Chem. Soc.*, 86 (1964) 964.
- 8 S. R. LANDAUER AND H. N. RYDON, *J. Chem. Soc.*, (1953) 2224.
- 9 N. KORNBLUM AND D. C. IFFLAND, *J. Am. Chem. Soc.*, 77 (1955) 6653.
- 10 J. V. MORTIMER AND P. L. GENT, *Nature*, 197 (1963) 789.
- 11 D. WHITE, *Nature*, 179 (1957) 1075.
- 12 W. GERRARD, H. R. HUDSON AND W. S. MURPHY, *J. Chem. Soc.*, (1964) 2314.

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