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## Gas chromatography of $C_6$ and $C_7$ cycloalkyl chlorides, cycloolefins, methylcycloalkanes, and related bicyclo[*n*.1.0] alkanes

Carbonium ion rearrangements in the reactions of cyclic alcohols with halogenating agents, or in the Lewis acid-catalysed isomerisation of cycloalkyl halides, can give rise to complex mixtures of products. For example, cyclohexylmethanol can yield up to eight different chlorides and six hydrocarbons, depending on the halogenating agent used. While a very brief report has been given of the separation of such chloride mixtures by gas–solid chromatography on graphitized thermal black[1], we have not been able to obtain satisfactory results by this procedure, and indeed certain of the products (1-methylcycloalkyl chlorides) are somewhat unstable at the recommended operating temperature of 120°. The difficulties experienced in separating all seven possible disubstituted cyclohexane isomers, $RC_6H_{10}X$, in related systems is well known in rearrangement chemistry, and a number of excellent papers on the separation of such systems exist[2]. In connection with our current studies of cycloalkyl rearrangements[3], we have investigated procedures for the analysis of the hydrocarbon and halide products that are formed in the reactions with chlorinating agents (HCl, $SOCl_2$, $COCl_2$, $BCl_3$, etc.) of a range of $C_6$ and $C_7$ cycloalkanols, *viz.*, cyclopentylmethanol, 1- and 2-methylcyclopentanols, cyclohexanol, cyclohexylmethanol, 1-, 2-, 3- and 4-methylcyclohexanols, and cycloheptanol.

*Experimental*

*Materials.* Alcohols, which were used in the preparation of the corresponding halides, were obtained commercially or prepared by the appropriate Grignard reaction. Each gave rise to a single peak on polyethylene glycol 400 (PEG-400) or squalane (sometimes after purification by preparative gas–liquid chromatography (GLC) on PEG-400) and its identity was confirmed by infrared and NMR analysis[4]. Olefins were obtained commercially. Bicyclo[3.1.0]hexane and bicyclo[4.1.0]heptane were prepared by the method of SIMMONS AND SMITH[5].

Chlorides were prepared by standard methods and gave satisfactory analytical data for C, H and Cl contents. Cyclopentyl, cyclohexyl and cycloheptyl chlorides were prepared by heating the corresponding alcohols under reflux with concentrated hydrochloric acid and calcium chloride[6]; cyclopentylmethyl and cyclohexylmethyl chlorides by heating the corresponding alcohols with thionyl chloride and pyridine[7]; and 1-methylcyclopentyl and 1-methylcyclohexyl chlorides by passing dry hydrogen chloride into the respective alcohols at 20–40°. The 2-, 3- and 4-methylcycloalkyl chlorides were obtained by thermal decomposition of their respective chloroformate esters at 150°[3,8]. Thus, *cis*-2-methylcyclopentyl chloroformate gave the *cis* (90.0%) and *trans* (10.0%) chlorides; *cis*-2-methylcyclohexyl chloroformate gave the *cis* (81.8%) and *trans* (18.2%) chlorides, from which preparative GLC on polyethylene glycol adipate gave *cis*-2-methylcyclohexyl chloride, $n_D^{20}$ 1.4627; *trans*-2-methylcyclohexyl chloroformate gave the *cis* (13.3%) and *trans* (86.7%) chlorides from which preparative GLC similarly gave *trans*-2-methylcyclohexyl chloride, $n_D^{20}$ 1.4577; 3-methylcyclohexyl chloroformate (*cis* 67%; *trans* 33%) gave the *cis* (52.3%)

and *trans* (47.7 %) chlorides; 4-methylcyclohexyl chloroformate (*cis* 37 %; *trans* 63 %) gave the *cis* (37.1 %) and *trans* (62.9 %) chlorides. The *cis* and *trans* isomers were identified, either as the pure compounds or as the major or minor components in mixtures, by integration coupled with half-band width measurement of the methine proton peaks in the $^1$H NMR spectra[4]. *Cis*- and *trans*-3-methylcyclopentyl chloride (10.8 %) were obtained together with the 2-isomers (36.6 %) and 1-methylcyclopentyl chloride (52.6 %) by isomerization of the latter with aluminium trichloride (0.05 mol. equiv.) at 50° for 3 h and purification by preparative GLC; the combined chlorides (found: C, 60.46; H, 9.40; Cl, 29.6 %; calculated for $C_6H_{11}Cl$: C, 60.76; H, 9.28; Cl, 29.95 %) revealed a broad peak that was assigned to the inseparable *cis*- and *trans*-3-methylcyclopentyl chlorides, lying between those due to the *cis*- and *trans*-2-methylcyclopentyl chlorides.

*Apparatus.* Analytical gas chromatography was performed on a Perkin-Elmer F-11 chromatograph with nitrogen as carrier gas and a flame ionization detector. The most efficient column found was a 50 m × 0.25 mm O.D. stainless-steel wall-coated capillary column containing silicone fluid MS 550. Optimum conditions for separations of the hydrocarbons and the chlorides were different:

(*a*) the hydrocarbons were analyzed at 20° with an inlet pressure of 20 p.s.i. and a medium-flow stream splitter (No. 18) giving a nitrogen flow-rate of *ca.* 2 ml/min (Fig. 1); and

(*b*) the cycloalkyl chlorides were analyzed at 35° with an inlet pressure of 19 p.s.i. and a low-flow stream splitter (No. 20) giving a nitrogen flow-rate of 1.5–2 ml/min (Fig. 2).

*Spectroscopy.* Infrared spectra of pure chloride isomers were recorded for liquid films on a Perkin-Elmer 157 spectrometer and were in agreement with those given

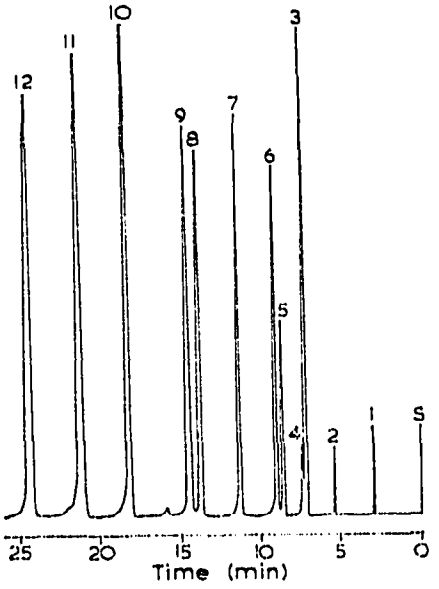


Fig. 1. Separation of $C_6$ and $C_7$ cycloolefins, methylcycloalkanes and bicyclo[*n*.1.0]alkanes on a silicone oil capillary column (conditions as in *Experimental* section). 1 = Diethyl ether; 2 = 3-methylcyclopentene; 3 = 1-methylcyclopentene; 4 = methylenecyclopentane; 5 = bicyclo[3.1.0]hexane; 6 = cyclohexene; 7 = methylcyclohexane; 8 = 3-methylcyclohexene and 4-methylcyclohexene (the analysis of these, and of 4-methylcyclopentene which is not given here, have been reported elsewhere[9]); 9 = methylenecyclohexane; 10 = 1-methylcyclohexene; 11 = cycloheptene; 12 = bicyclo[4.1.0]heptane.

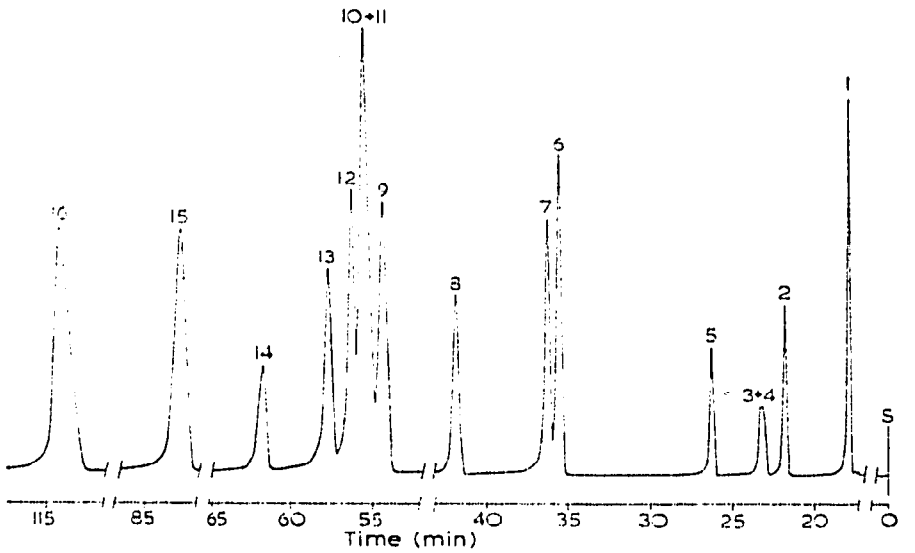


Fig. 2. Separation of $C_6$ and $C_7$ cycloalkyl chlorides on a silicone oil capillary column (conditions as in *Experimental* section). 1 = 1-Methylcyclopentyl chloride; 2 = *trans*-2-methylcyclopentyl chloride; 3 = *cis*-3-methylcyclopentyl chloride; 4 = *trans*-3-methylcyclopentyl chloride; 5 = *cis*-2-methylcyclopentyl chloride; 6 = cyclohexyl chloride; 7 = cyclopentylmethyl chloride; 8 = 1-methylcyclohexyl chloride; 9 = *trans*-2-methylcyclohexyl chloride; 10 = *cis*-3-methylcyclohexyl chloride; 11 = *trans*-4-methylcyclohexyl chloride; 12 = *trans*-3-methylcyclohexyl chloride; 13 = *cis*-4-methylcyclohexyl chloride; 14 = *cis*-2-methylcyclohexyl chloride; 15 = cyclohexylmethyl chloride; 16 = cycloheptyl chloride.

in the literature, as indicated in Table I. $^1$H NMR spectra were recorded on a Perkin-Elmer R-10 60 MHz spectrometer with tetramethylsilane as the internal standard.

*Results and discussion*

A silicone oil capillary column was found to be the most effective of a number that were investigated for the separation of the isomeric $C_6$ and $C_7$ cycloalkyl chlorides specified in Table I. Of the $C_6$ compounds, only the *cis*- and *trans*-3-methylcyclopentyl chlorides were inseparable from each other. In the $C_7$ series, only the *cis*-3- and *trans*-4-methylcyclohexyl chlorides had identical retention times; other workers have reported a similar difficulty in the analysis of mixtures of *cis*-3- and *trans*-4-substituted cyclohexyl derivatives[2]. The following stationary phases also afforded no separation of these particular pairs of isomers: polyethylene glycol, polyethylene glycol adipate, squalane, dibutyl D-tartrate, oxydipropionitrile, micrographite, silicone–bentone (the last having proved valuable for the analysis of certain acyclic pentyl halides)[17].

On silicone oil, the chlorides eluted in increasing order of boiling-point, and it is interesting to note that in both the $C_6$ and $C_7$ series the *trans*-2-methyl was the first and the *cis*-2-methyl the last of the secondary methylcycloalkyl chlorides to elute. Infrared results are reported in the literature for many of the isomers analyzed here and are helpful in their identification in mixtures (see the references in Table I). $^1$H NMR results are, however, incomplete or unreported for many of these chlorides and our results are therefore now included in Table I as a further aid to identification.

Table II gives retention data for hydrocarbon by-products that are frequently formed together with the cycloalkyl chlorides in question. These are mainly the

TABLE I

RELATIVE RETENTION TIMES ON A SILICONE OIL CAPILLARY COLUMN[a] AND SPECTROSCOPIC DATA FOR $C_6$ A

| *Compound* | $t_R$ *(min)* | *Rel. retention time*[b] | *Infrare referenc* |
|---|---|---|---|
| 1-Methylcyclopentyl chloride | 17.8 | 0.51 | 10 |
| *trans*-2-Methylcyclopentyl chloride | 21.7 | 0.62 | — |
| *cis*-3-Methylcyclopentyl chloride | 24.0 | 0.66 | — |
| *trans*-3-Methylcyclopentyl chloride | 24.0 | 0.66 | — |
| *cis*-2-Methylcyclopentyl chloride | 26.3 | 0.74 | — |
| Cyclohexyl chloride | 35.5 | 1.00 | 11 |
| Cyclopentylmethyl chloride | 36.2 | 1.02 | 7 |
| 1-Methylcyclohexyl chloride | 42.0 | 1.17 | 12 |
| *trans*-2-Methylcyclohexyl chloride | 54.3 | 1.53 | 13, 14 |
| *cis*-3-Methylcyclohexyl chloride | 55.3 | 1.55 | 12 |
| *trans*-4-Methylcyclohexyl chloride | 55.3 | 1.55 | 12 |
| *trans*-3-Methylcyclohexyl chloride | 56.2 | 1.57 | 12 |
| *cis*-4-Methylcyclohexyl chloride | 57.7 | 1.61 | 12 |
| *cis*-2-Methylcyclohexyl chloride | 61.7 | 1.73 | 13, 14 |
| Cyclohexylmethyl chloride | 82.7 | 2.32 | 15 |
| Cycloheptyl chloride | 114.0 | 3.17 | 16 |

[a] Optimum conditions as given in *Experimental* section.
[b] Cyclohexyl chloride = 1.00.
[c] m = multiplet, d = doublet, s = singlet, h.b.w. = half-band width (of methine protons).

TABLE II

RELATIVE RETENTION TIMES FOR $C_6$ AND $C_7$ CYCLOOLEFINS, METHYLCYCLOALKANES AND BICYCLO[*n*.1.0]ALKANES ON A SILICONE OIL CAPILLARY COLUMN[a]

| *Compound* | $t_R$ *(min)* | *Rel. retention time*[b] |
|---|---|---|
| 3-Methylcyclopentene | 5.5 | 0.49 |
| 1-Methylcyclopentene | 7.2 | 0.63 |
| Methylenecyclopentane | 7.3 | 0.65 |
| Bicyclo[3.1.0]hexane | 8.5 | 0.76 |
| Cyclohexene | 9.0 | 0.80 |
| Methylcyclohexane | 11.2 | 1.00 |
| 3-Methylcyclohexene | 13.8 | 1.23 |
| 4-Methylcyclohexene | 13.8 | 1.23 |
| Methylenecyclohexane | 14.5 | 1.29 |
| 1-Methylcyclohexene | 18.2 | 1.64 |
| Cycloheptene | 21.2 | 1.89 |
| Bicyclo[4.1.0]heptane | 24.3 | 2.17 |

[a] Optimum conditions as given in *Experimental* section.
[b] Methylcyclohexane = 1.00.

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| *NMR chemical shift* (τ)[c] |
|---|
| o–8.50 (ring $CH_2$ groups, m), 8.36 ($CH_3$, s) |
| 7 (CH,m,h.b.w. = 16.0 Hz), 7.60–8.60 (ring $CH_2$ groups, m), 9.00 ($CH_3$,d, $J_{HCCH}$ = 7.0 Hz) |
| 5 (CH,m,h.b.w. = 7.0 Hz), 7.60–8.60 (ring $CH_2$ groups, m), 8.94 ($CH_3$,d, $J_{HCCH}$ = 6.9 Hz) |
| 5 (CH,m,h.b.w. = 15 Hz), 7.80–8.90 (ring $CH_2$ groups, m) |
| 5 ($CH_2$,d, $J_{HCCH}$ = 6.0 Hz), 7.60–9.00 (ring $CH_2$ groups, m) |
| 5–8.80 (ring $CH_2$ groups, m), 8.43 ($CH_3$, s) |
| 5 (CH,m,h.b.w. = 17.0 Hz), 7.80–8.80 (ring $CH_2$ groups, m), 8.95 ($CH_3$,d, $J_{HCCH}$ = 6.0 Hz) |
| 5 (CH,m,h.b.w. = 17.1 Hz), 7.70–9.20 (ring $CH_2$ groups, m), *ca.* 9.10 ($CH_3$,d, $J_{HCCH}$ *ca.* 6.0 Hz) |
| 5 (CH,m,h.b.w. = 20.6 Hz), 7.70–9.30 (ring $CH_2$ groups, m), *ca.* 9.10 ($CH_3$,d, $J_{HCCH}$ *ca.* 6.5 Hz) |
| 5 (CH,m,h.b.w. = 8.6 Hz), 7.70–9.20 (ring $CH_2$ groups, m), *ca.* 9.10 ($CH_3$,d, $J_{HCCH}$ *ca.* 6.0 Hz) |
| 3 (CH,m,h.b.w. = 8.6 Hz), 7.70–9.30 (ring $CH_2$ groups, m), *ca.* 9.10 ($CH_3$,d, $J_{HCCH}$ *ca.* 6.5 Hz) |
| 5 (CH,m,h.b.w. = 7.7 Hz), 8.00–8.80 (ring $CH_2$ groups, m), 9.02 ($CH_3$d, $J_{HCCH}$ = 6.0 Hz) |
| 5 ($CH_2$, d, $J_{HCCH}$ = 6.0 Hz), 8.00–9.20 (ring $CH_2$ groups, m) |
| 5 (CH, m, h.b.w. = 17 Hz), 7.80–8.80 (ring $CH_2$ groups, m) |

corresponding olefins, for which a number of complete analyses have been reported (see, for example, references 9 and 18), together with bicyclo[3.1.0]hexane, bicyclo-[4.1.0]heptane, methylcyclopentane and methylcyclohexane.

The retention data given in Tables I and II are for the optimum conditions for analysis of the hydrocarbons and cycloalkyl chlorides separately. For complete analysis of the total products, the column conditions should be changed after the hydrocarbons have eluted.

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