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Note

THERMAL DECOMPOSITION TO DEHALOGENATION OF α-HALOKETONES BY GLC

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INTRODUCTION

Dehalogenation of α-haloketones has been done effectively by various procedures; sodium borohydride and metal salts [1] zinc and acetic acid [2], lithium iodide and boron trifluoride [3], sodium dithionite [4], sodium iodide and sulfuric acid [5], titanium(III) chloride [6], diisobutylaluminum hydride and tin(II) chloride [7] and sodium hydrogentelluride [8] etc. The author has been encouraged by these publications to study the dehalogenation of α-haloketones by sodium borohydride and metal salts and found that α-haloketones effect thermal decomposition to dehalogenation. Some conditions in their thermal decomposition were then studied and the results are reported. For gas chromatography, glass columns or glass open tublar capillary columns have been widely used to avoid thermal decomposition of the samples in the analyses of organic compounds or natural products. Although the procedures have been known to chromatographic chemists, the decompositions of organic compounds on GLC columns, have rarely been published. A few reports have been published on the GLC analyses of chloroacetophenone [9,10].

EXPERIMENTAL

Liquid phase, samples and apparatus

The liquid phase, silicone KF-54 of guaranteed grade obtained from Shinetsu Chemical Co. (Tokyo, Japan), was used without any purification. α-Chloroacetophenone, α-bromoacetophenone, α-bromo-*p*-methylacetophenone were obtained from Aldrich Chemical Co. (Milwaukee, WI, U.S.A.) and 2-chlorocyclohexanone, methyl 2-chloropropionate and 2-chloroacetamide obtained from Nakarai Chemical Co. (Kyoto, Japan), which were used after purification.

A Shimadzu Model GC-5A gas chromatograph equipped with a flame ionization detector was used.

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Chromatographic procedure

The separation column was a 1.5 m × 3 mm ID stainless steel U-tube packed with acid-washed Sil-O-Cel C_{22} firebrick (John Manville, Corp. Denver, CO, U.S.A.), 60–80 mesh support coated with 20% (w/w) silicone KF-54. The column temperature was 170 or 200°C and the injector temperature was 200, 250 or 350°C, respectively. Nitrogen was used as the carrier gas (flow rate, 5 ml $\min^{-1}$).

RESULTS AND DISCUSSION

As shown in Table 1, α-haloacetophenones, α-chloroacetophenone, α-bromoacetophenone and α-bromo-*p*-methylacetophenone showed little thermal decomposition to dehalogenation at 170°C column temperature and 200°C injector temperature, and they are almost stable at this temperature. The other α-haloketones or α-halocarbonyl compounds were entirely stable at the above column and injector temperatures. Whereas, as shown in Table 2, α-haloacetophenone clearly effected thermal decomposition to acetophenone and α-chloroacetophenone afforded acetophenone to the following amounts: 25% at column temperature 200°C, injector temperature 250°C, 50% at column temperature 200°C, injector temperature 350°C, α-bromoacetophenone gave 86% acetophenone at column temperature 200°C, injector temperature 250°C, 95% at column temperature 200°C, injector temperature 350°C, and α-bromo-*p*-methylacetophenone gave 85% *p*-methylacetophenone at column temperature 200°C, injector temperature 250°C, 92% at column temperature 200°C, injector temperature 350°C. According to the results, α-haloacetophenones are found to thermally decompose to acetophenone at high injector temperature. Further, whereas the thermal decompositions of these α-haloacetophenones were not detected by GC with glass columns and glass injector ports, at column temperature 200°C, at injector temperature 300°C, the above decompositions were

TABLE 1

GLC of α-halocarbonyl compounds [a]

GLC retention and decomposition ratio			
α-Chloroacetophenone	(7.8 min, 98%),	acetophenone	(3.0 min, 2.0%)
α-Bromoacetophenone	(13.2 min, 90.7%),	acetophenone	(3.0 min, 9.3%)
α-Bromo-*p*-methyl acetophenone	(18.6 min, 91.7%),	*p*-methylacetophenone	(4.6 min, 8.3%)
2-Chlorocyclohexanone	(2.8 min)	–	
Methyl 2-chloropropionate	(0.8 min)	–	
2-Chloroacetamide	(4.2 min)	–	

[a] Liquid phase: silicone KF-54; column temperature: 170°C; injector temperature: 200°C; column length: 1.5 m.

TABLE 2

Decomposition of α-halocarbonyl compounds at 250 or 350°C [a]

GLC retention and decomposition ratio				Injector temperature (°C)
α-Chloroacetophenone	(2.2 min, 50%),	acetophenone	(0.8 min, 50%)	350
α-Bromoacetophenone	(3.0 min, 5%),	acetophenone	(0.8 min, 95%)	350
α-Bromo-*p*-methylacetophenone	(3.4 min, 8%),	*p*-methylacetophenone	(1.4 min, 92%)	350
α-Chloroacetophenone	(2.4 min, 75%),	acetophenone	(1.0 min, 25%)	250
α-Bromoacetophenone	(3.2 min, 14%),	acetophenone	(1.0 min, 86%)	250
α-Bromo-*p*-methylacetophenone	(3.6 min, 15%),	*p*-methylacetophenone	(1.4 min, 85%)	250

[a] Liquid phase: silicone KF-54; column temperature: 200°C; column length: 1.5 m.

obtained on a metal column and metal injector. The other compounds, 2-chlorocyclohexanone, methyl 2-chloropropionate, and 2-chloroacetamide would not thermally decompose to their corresponding parent ketones and carbonyl compounds. α-Haloalkanones are difficult to dehalogenate with sodium iodide and chlorotrimethyl silane [12] and this may coincide with the above results. This result may be understood by the following explanation. 2-Chlorocyclohexanone has an electron donating alkyl group (Hammett σp, -0.17) [11] at the α-carbon and carbonyl carbon; methyl 2-chloropropionate has an electron donating methyl group (σp, -0.17) at the α-carbon and an electron donating methoxy group (σp, -0.27) at the carbonyl carbon and 2-chloroacetamide has an electron donating amino group (σp, -0.66) at the carbonyl carbon. According to the results for these compounds, the α-halogens activated by the carbonyl (electron attractive group, σp, 0.44) are deactivated by the inductive effect of substituents at α-carbon or carbonyl carbon mentioned above, and the 2-chlorocyclohexanone, methyl 2-chloropropionate and 2-chloroacetamide are stable at high temperatures and could not thermally decompose to dehalogenation at this high temperature. From the results, dehalogenation of α-haloketones may be obtained by the thermal catalytic thermolysis by the metal, when α-carbon of the α-haloketone is not deactivated or the electron attracting ability of the carbonyl group is not deactivated by the substituent at the α-carbon or carbonyl carbon. Consequently, the thermal dehalogenation of α-haloketones is due to the substituent effect of the α-carbon and carbonyl carbon and also due to metallic catalytic action.

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