Separation of Silylated Oxime Isomers by High Resolution Gas Chromatography

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Synopsis. The stereoisomers of 2-butanone *O*-trimethylsilyloxime were observed as separate peaks, the intensity ratio being 1 : 3, by high resolution GC equipped with a capillary column. The peak with intensity 3 was assigned to the *Z* isomer of oxime bond and the intensity ratio corresponded to the stereoisomer ratio of 2-butanone oxime. Silanes including plural oxime groups also gave separate stereoisomer peaks corresponding to the isomer ratio of 2-butanone oxime.

It is well known that an oxime bond can take two isomeric structures, *E* and *Z* form. The stereochemistry has been actively studied by use of ^{1}H NMR.[1—3] Meanwhile, GC is also a very useful tool to analyze stereoisomeric compounds quantitatively and a lot of results have been reported.[4—8] In particular, a capillary column brought a remarkable development on high resolution GC. It was suggested that various stereoisomers, which had been observed as only one fraction in the case of a packed column, could be separated by the capillary column. In this paper, we would like to report the separation and the quantitative determination of stereoisomers of *O*-silylated 2-butanone oxime using high resolution GC equipped with the capillary column.

Experimental

Reagents. 2-Butanone oxime (Toa Gousei Co., Ltd.), triethylamine and hexane of HPLC grade (Tokyo Chemical Co., Ltd.) were used without further purification. Chlorosilanes were obtained as chemical grade from Shin-Etsu Chemical Co., Ltd.

Apparatus and Analytical Conditions. GC was measured with a Hewlett Packard Model HP5890 equipped with a J&W Scientific Model DB-1701 megabore capillary column, 0.53 mm i.d. ×30 m, coated with silicone gum consisting of 14% of (3-cyanopropyl)phenylsiloxane unit and 86% of dimethylsiloxane unit. Analytical conditions were set up to attain the complete separation of a cis and a trans isomer of 2-heptene as summarized in Table 1.

The ^{1}H NMR spectra were measured on a JEOL PMX-60SI using DMSO-d_6 as a solvent and TMS as an internal standard.

Procedure for Preparation of *O*-Silylated 2-Butanone Oxime. A solution of 2-butanone oxime (1.04 g, 0.012 mol) and triethylamine (1.01 g, 0.01 mol) in hexane (10 ml) was placed in four necked flask charged with N_2. After chlorotrimethylsilane (1.08 g, 0.01 mol) was added into the solution at room temperature, the mixture was heated under stirring at 80 °C for 1 h. Then, the hexane layer was separated from triethylamine hydrochloride by filtration. An analytical sample of 2-butanone *O*-trimethylsilyloxime was obtained by evaporation of hexane, followed by distillation under reduced pressure. The other *O*-silylated oximes were also prepared according to the same procedure.

Result and Discussion

Gas Chromatographic Analysis of *O*-Silyloxime. The analysis of 2-butanone *O*-trimethylsilyloxime by DB-1701 column gave two separate fractions having an intensity ratio of 1 : 3 as shown in Fig. 1. As each fraction gave same MS fragment peaks, it was concluded that two fractions arose from two stereoisomers of 2-butanone *O*-trimethylsilyloxime, *E* and *Z* form.

Meanwhile, a semiempirical calculation using AM1 method gave a prediction that, of two stereoisomers of 2-butanone oxime, a *Z* isomer is predominant over an *E* isomer and the ratio of *Z* to *E* is 3 to 1. The ^{1}H NMR of 2-butanone oxime in DMSO-d_6 also showed that the *Z*/*E* ratio was 3 : 1.

As it is considered that the configuration of carbon–nitrogen bond of the oxime is not affected in the substitution process of hydrogen atom with trimethylsilyl group, the stereochemistry of trimethylsilylated derivative may be corresponding to that of starting 2-butanone oxime. Accordingly the peak eluted earlier should be corresponding to the *E* isomer and the *Z*/*E* ratio should be 3 : 1.

On the other hand, the separation of stereoisomers

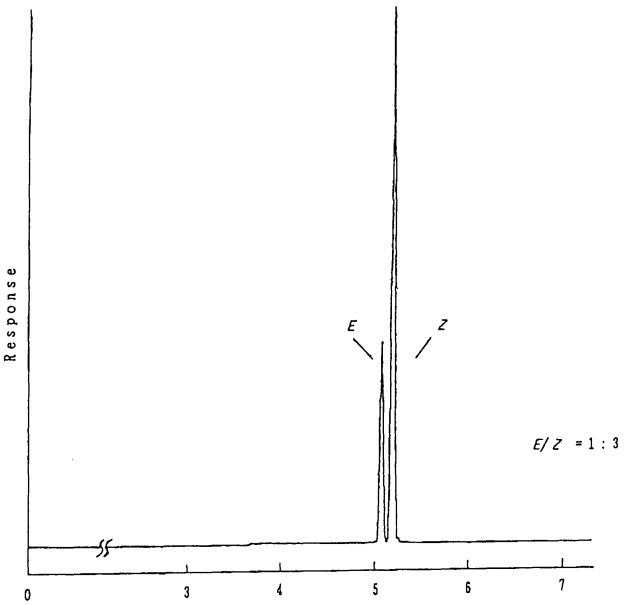

Fig. 1. Gas chromatogram of 2-butanone *O*-trimethylsilyloxime. Column; DB-1701, 0.53 mm i.d.×30 m. Chart speed; 10 cm min^{-1}.

Table 1. Analytical Conditions

Column	Megabore column (DB-1701)
Column liquid phase	14% Cyanopropyl phenyl–86% dimethylpolysiloxane
i.d.	0.53 mm
Film thickness	1 μm
Column length	30 m
Column temp	50—250°C
Rate	10°C min^{-1}
Split ratio	1/25

of 2-butanone oxime by GC was unsuccessful. By DB-WAX capillary column coated with more polar poly(ethylene glycol) as well as by DB-1701 megabore capillary column, separate GC peaks were not observed.

In the case of 2-butanone *O,O'*-(dimethylsilanediyl)-dioxime, three stereoisomers reflecting the isomer ratio of the oxime should be present and the ratio should be calculated as shown in Table 2. It is also predicted that 2-butanone *O,O',O''*-(methylsilylidyne)trioxime and 2-butanone *O,O',O'',O'''*-silanetetrayltetraoxime should also give four and five isomers, respectively. In practice, the GC peaks of 2-butanone *O,O',O''*-(methylsilylidyne)trioxime were observed as shown in Fig. 2. The observed results are also summarized in Table 2. The peak ratios almost agreed with the calculated values, respectively. These results indicate that the isomers of the *O*-silylated oxime are faithfully reflecting the stereochemistry of the starting oxime bond, even in 2-butanone *O,O',O'',O'''*-silanetetrayltetraoxime.

Furthermore, 2-butanone oxime also reacted readily with silanes having a bulky group, such as a *t*-butyl or a phenyl group. The difference of reaction rate between *E* and *Z* isomer was not recognized and *O*-silylated oximes

Table 2. GC Retention Time and Relative Intensity of Silane Compounds

Sample	Retention time/min	Peak area %	Calculated peak area (%)
$Me_3Si(BO)$ [a]	5.00	24.3	25
	5.09	75.7	75
	11.00	6.0	6.3
$Me_2Si(BO)_2$ [a]	11.19	37.3	37.5
	11.35	56.7	56.2
	16.98	1.7	1.6
$MeSi(BO)_3$ [a]	17.18	13.6	14.1
	17.39	40.9	42.2
	17.56	43.8	42.2
			0.4[b]
	20.75	3.0	4.7
$Si(BO)_4$ [a]	20.96	19.6	21.1
	21.17	43.0	42.2
	21.36	34.4	31.6

a) BO=–ON=C(Me)Et. b) Five peaks were suggested by calculation.

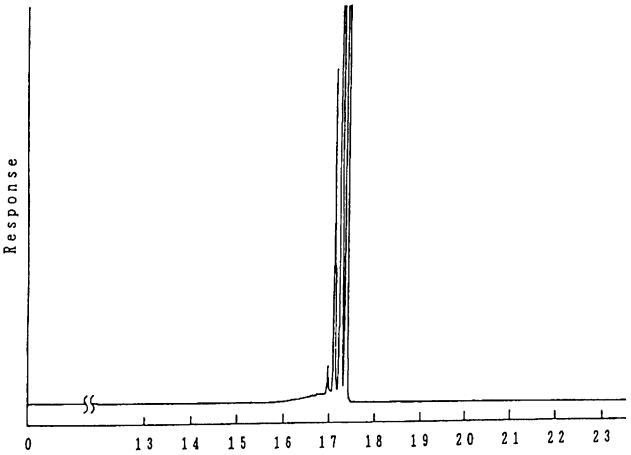

Fig. 2. Gas chromatogram of 2-butanone *O,O',O''*-(methylsilylidyne)trioxime. Column; DB-1701, 0.53 mm i.d.×30 m. Chart speed; 10 cm min^{-1}.

corresponding to the sterochemistry of starting oxime were also given.

Conclusion

The *E* and *Z* isomer of *O*-silylated 2-butanone oximes were successfully separated by use of high resolution GC equipped with capillary column. The ratios of stereoisomers reflected that of the starting oxime. It was also proved that the silanes substituted with two or more of 2-butanone oxime give separate peaks corresponding to the steroisomers of oxime and the peak ratios are reflecting the stereochemistry of starting oxime.

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