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SEPARATION OF ISOMERS BY DISTILLATION IN THE PRESENCE OF HOST COMPOUND

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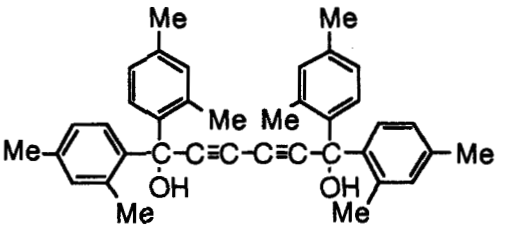
Abstract Selective inclusion complexation of a volatile guest compound with a crystalline host compound in the solid state occurs efficiently by mixing both components without using any solvent. When the phenomena is combined with distillation procedure, separation of isomers which have the same or the similar boiling point by distillation is achieved.

Introduction

The technique of isolation, separation, and purification of compounds is important in laboratory and industry. We have been studied separation of various kinds of isomers by inclusion complexation with host compound **1**-**4**.[1] Since the host compound **1**–**4** has a high molecular recognition ability for guest compounds and includes one isomer selectively, isomers can be separated by using the inclusion complexation. The inclusion complexation has been carried out so far by recrystallization of host and guest compound from solvent, such as ether, toluene, and methanol. Recently we have found that the inclusion complexation occurs in the absence of solvent. When finely powdered host compound and a mixture of volatile isomers are mixed in the absence of solvent, one isomer is included selectively by the host to give an inclusion complex, from which pure isomer can be separated by distillation. By a combination of the selective inclusion complexation in the solid state and distillation procedure, separation of isomers which have the same or the similar boiling point can be achieved efficiently by simple distillation technique. The host compound is recovered unchanged and can be used again and again.

This new separation method might be useful not only in laboratory but also in industry, since this method is simple and economical.



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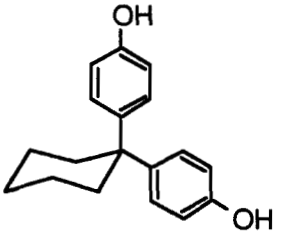
a: X=H

b: X=Me



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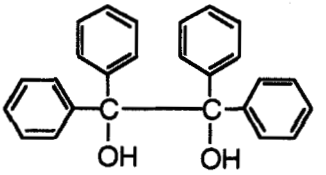

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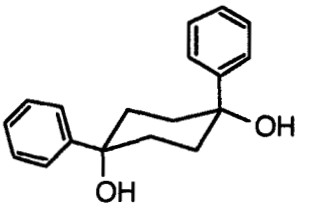

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Experimental Section

For example, the host, 1,1,4,4-tetrakis(2,4-dimethylphenyl)-but-2-yn-1,4-diol (**1b**) (1.27 g, 2.4 mmol) was combined with a mixture of 1,4-butanediol (**5**) (bp 230 ℃) (0.22 g, 2.4 mmol) and 1,3-butanediol (**6**) (bp 203-204 ℃) (0.29 g, 3.2 mmol) and then heated in Kugelrohr at 100 ℃/2 mmHg to give **6** of 100% purity (0.29 g, 100% yield). Further heating of the residue at 180 ℃/2 mmHg gave **5** of 100% purity (0.21 g, 97% yield).

When the purity of isomer obtained by one distillation procedure is not enough, pure isomer can be obtained easily by repeating the procedure. For instance, **1b** was combined with a mixture of *cis*- (**15**) and *trans*-2,6-dimethylcyclohexanone (**16**) (**15**:**16**=81:19) and then heated in Kugelrohr at 90 ℃/16 mmHg to give **16** of 29% purity. Further heating of the residue at 150 ℃/2 mmHg gave **15** of 85% purity. By repeating four times the procedure, **15** of 92% purity was distilled from an inclusion complex with **1b** in 39% yield.

By the same procedure, various types of isomers were separated efficiently into pure isomers as shown in Table 1-3. In the Tables, only the isomer which forms inclusion

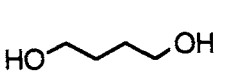
complex with the host and then distils at a relatively high temperature is indicated..

Results and Discussion

On mixing powdered host and a mixture of volatile isomers, one isomer was included selectively by the host and another isomers were not. Upon heating the mixture in *vacuo*, uncomplexed isomers distilled at relatively low temperature, and the isomer which had been included by the host in inclusion complex distilled at relatively high temperature. The new separation method is efficiently applicable to separation of various kinds of isomers of which the separation in the usual fashion is not easy because of the similarity in boiling points. The separation of 1,4- (**5**) and 1,3-butanediol (**6**) is one of most effective examples. The host **1b** recognized the difference between the straight alkyl chain of **5** and the branched alkyl chain of **6**, and accommodated the former in an inclusion complex exclusively.[2] In this case, sterically less bulky isomer **5** would form a more thermodynamically stable inclusion complex with the host compound. The colorless needle crystals of a 1:1 inclusion complex of **1b** and **5** which had been prepared by recrystallization of both components from 2-propanol, showed hydrogen bonded broad νOH absorption at 3200 cm^{-1} in an IR spectrum, although **1b** shows a sharp νOH absorption at 3520 cm^{-1}. The data suggest that the hydrogen bond between the OH group of **1b** and the OH group of **5** plays an important role in the complex formation. Although the inclusion crystal decomposes to the components at the melting point 174-177 ℃, it is stale enough to be kept unchanged blow that temperature during the distillation to separate the uncomplexed **6**. After the removal of **6**, the distillation temperature is raised up to the melting point and complexed **5** is released from the inclusion complex. This is the principle of the separation of isomers by distillation in the presence of host compound.

When the purity of isomer obtained by one distillation procedure is not high, pure isomer can be obtained by repeating the procedure.

Separation of Structural Isomers. Although separation of β- (**7**) (bp 144 ℃) and γ-picoline (**8**) (bp 145 ℃) is important in industry, it is not easy and wastes much energy to get each isomer in pure state by usual distillation.[3] The separation of **7** and **8** can be achieved efficiently by the newly developed method. When the host **2** was used for the separation of a 7:3 mixture of **7** and **8**, **7** of 90% purity was obtained by repeating three times the procedure. On the other hand, when the host **3** was used for the separation of a 3:7 mixture of **7** and **8**, **8** of 99% purity was obtained by repeating four times the procedure. Separation of *m*- (**9**) (bp 202 ℃) and *p*-cresol (**10**) (bp 202.5 ℃) is also



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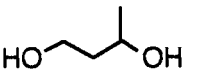

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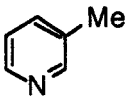

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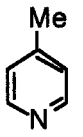

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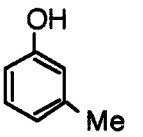

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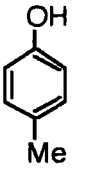

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important in industry.[4] It is also achieved successfully and **9** of 90% purity was obtained from a 1:1 mixture of **9** and **10**. The results of separation of structural isomers are summarized in Table 1.

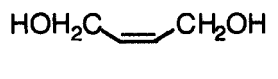
Table 1. Separation of structural isomers by fractional distillation in the presence of host compound

Host	Guest (ratio)	Distillation times repeated	Product [a]	Yield (%)	Purity (%) [b]
1b	**5**:**6** (43:57)	1	**5**	97	100
2	**7**:**8** (70:30)	3	**7**	57	90
3	**7**:**8** (30:70)	4	**8**	39	99
2	**9**:**10** (50:50)	5	**9**	32	90

[a] Only the isomer which forms inclusion complex with the host used and then distils at relatively high temperature is indicated.

[b] Purity was determined by GC.

Separation of Stereoisomers. Separation of *cis*- (**11**) (bp 132 °C/16 mmHg) and *trans*-2-butene-1,4-diol (**12**) (bp 131 °C/16 mmHg) was achieved and **12** of 77% and 83% purity were obtained by using **1b** and **4**, respectively.[4,5] 3,5-cyclohexanone is commercially available as a 89:11 mixture of *cis*- (**13**) (bp 182-183 °C) and *trans*-isomer (**14**) (bp 180-181 °C),[2,4] and 2,6-cyclohexanone is commercially available as a 81:19 mixture of *cis*- (**15**) (bp 170-171 °C) and *trans*-isomer (**16**) (bp 25 °C/0.1 mmHg). Separations of **13** and **14**, and **15** and **16** were achieved in a excellent efficiency by the



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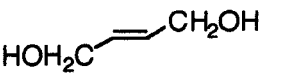

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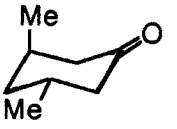

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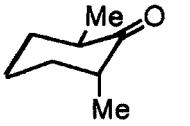

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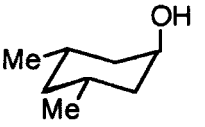

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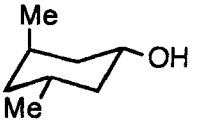

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distillation procedure.[4,6] Interestingly, this method is efficiently applicable to the separation of a mixture of three isomers (**17** (bp 79-80 °C/17 mmHg), **18** (bp 83-84 °C/17 mmHg), **19** (bp 84 °C/17 mmHg)). The results of separation of stereoisomers are summarized in Table 2.

Table 2. Separation of stereoisomers by fractional distillation in the presence of host compound

Host	Guest (ratio)	Distillation times repeated	Product [a]	Yield (%)	Purity (%)[b]
1b	**11**:**12** (50:50)	1	**12**	53	77
4	**11**:**12** (50:50)	1	**12**	38	83
1a	**13**:**14** (89:11)	1	**13**	64	97
1b	**15**:**16** (81:19)	2	**15**	39	92
1a	**17**:**18**:**19** (24:59:18)	2	**18**	27	90

[a] Only the isomer which forms inclusion complex with the host used and then distils at relatively high temperature is indicated.

[b] Purity was determined by GC.

Separation of cyclohenanol and cyclohexanone. Separation by usual distillation of cyclohexanol (**20**) (bp 161 ℃) and cyclohexanone (**21**) (bp 156 ℃) which are produced by air-oxidation of cyclohexane in industry, is not easy and wastes too much energy.[7] However, separation of **20** and **21** can easily be accomplished by the distillation method in the presence of host compound.

20 **21**

Heating of a 49:51 mixture of **20** and **21** in the presence of the host **2** gave firstly the uncomplexed **21** of 70% purity by distillation at 70 ℃/2 mmHg and secondly the complexed **20** of 69% purity by distillation at 150 ℃/2 mmHg. When the separation was repeated four times, **20** of 99% purity was obtained in 43% yield (Table 3). **21** of 99% purity was also obtained by repeating four times the distillation procedure in the presence of **1a**.

Table 3. Separation of cyclohexanol (**20**) and cyclohxanon (**21**) by fractional distillation in the presence of host compound

Host	Guest (ratio)	Distillation times repeated	Product [a]	Yield (%)	Purity (%) [b]
2	**20**:**21** (49:51)	4	**20**	43	99
1a	**20**:**21** (49:51)	4	**21**	23	99

[a] Only the isomer which forms inclusion complex with the host used and then distils at relatively high temperature is indicated.
[b] Purity was determined by GC.

Acknowledgment

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