July, 1990] © 1990 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 63, 2127—2128 (1990) 2127

Optical Resolution of Arsine Oxides by Complexation with Optically Active [1,1′-Binaphthyl]-2,2′-diol

Koji Mori and Fumio Toda*
Department of Industrial Chemistry, Faculty of Engineering,
Ehime University, Matsuyama, Ehime 790

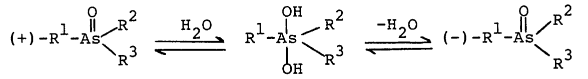
(Received February 9, 1990)

Synopsis. Some dialkylarylarsine oxides were resolved efficiently by complexation with optically active [1,1′-binaphthyl]-2,2′-diol.

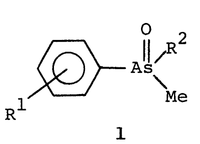
As we are aware, only one attempt on the optical resolution of arsine oxide has been reported by L. Horner and his coworker.[1)] They have shortly reported that the resolution is very difficult because optically active arsine oxide rapidly racemizes in the presence of a small amount of water through the equilibrium shown in Scheme 1. Our continuous successes in the optical resolution of a wide variety of organic compounds by complexation with optically active host compounds prompted us to try the optical resolution of arsine oxide.[2)] We now report efficient optical resolution of some dialkylarylarsine oxides (**1**) by complexation with optically active [1,1′-binaphthyl]-2,2′-diol (**2**).[3)]

The enantioselective complexation of racemic **1** with (−)-host (**2**) in acetone–hexane gave a 1:1 inclusion compound (**3**) of (+)-**1** and **2** as crystals in the yield shown in Table 1. Since the (+)-**1** was not isolated in pure state from **3** without racemization, the optical purity was determined for the (+)-**1** in **3**, by measuring quickly the ^{1}H NMR spectrum of a freshly prepared $CDCl_3$ solution of **3** in the presence of the chiral shift reagent, (−)-1,6-bis(*o*-chlorophenyl)-1,6-diphenyl-2,4-hexadiyne-1,6-diol (**4**),[4)] (Table 1).

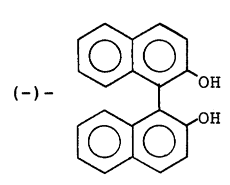
The optical purity of the (+)-**1** is not very high, probably because of an easy racemization. Half-life time of the ethyl group substituted ones (**1e** and **1g**), ca. 4—5 min in $CDCl_3$ at 37 °C, was much shorter than that of isopropyl group substituted ones (**1b**, **1d**, **1f**,



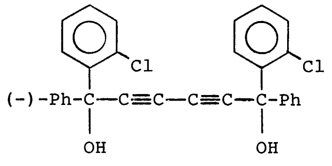
Scheme 1.



1



2



4

Table 1. Yield and Optical Purity of the (+)-**1** in **3** and Melting Point of **3**

	Arsine oxide (**1**)		Mp/°C of **3**[a)]	(+)-**1**	
	R¹	R²		Yield/%[b)]	% ee[c)]
1a	H	Et	210—211	78	—[d)]
1b	H	*i*-Pr	170—172	52	65
1c	*o*-Me	Et	188—189	91	0
1d	*o*-Me	*i*-Pr	167—168	64	64
1e	*m*-Me	Et	175—176	91	42
1f	*m*-Me	*i*-Pr	144—145	50	64
1g	*p*-Me	Et	155—158	57	40
1h	*p*-Me	*i*-Pr	163—165	38	65

a) **3** is a 1 : 1 inclusion compound of optically active **1** and **2**. b) Yield was calculated based on **3** formed. c) Optical purity of (+)-**1** was determined by measuring ^{1}H NMR spectrum of **3** in the presence of **4** in $CDCl_3$. d) Optical purity was not determined due to an insolubility of the complex (**3a**) in $CDCl_3$.

Table 2. Relationship between the Chemical Shift Value of the Me Signal of Racemic **1** and the Ratio of **4** to **1**

Arsine oxide (**1**)	Chemical shift value δ/ppm[a)]		
	Molar ratio of **4** to racemic **1**		
	0	1	2
1a	1.800	1.617 1.650	1.533 1.567
1b	1.827	1.617 1.650	1.533 1.587
1c	1.850	1.633 1.667	1.550 1.617
1d	1.917	1.750 1.783	1.667 1.717
1e	1.800	1.667	1.440 1.493
1f	1.833	1.583 1.600	1.450 1.493
1g	1.783	1.583 1.600	1.500 1.550
1h	1.767	1.650 1.677	1.550 1.600

a) All the signals are of the Me protons on the As atom.

and **1h**), ca. 35 min under the same conditions. The arsine oxide which is substituted with relatively more bulky alkyl group would resist against such hydration as shown in Scheme 1 and the rate of the racemization would be relatively slower. In any way, the real optical purity of the (+)-**1** in **3** would be higher than those estimated by ^{1}H NMR spectroscopy. It is not clear, however, why the resolution method is not effective for **1c** (Table 1).

The chemical shift values of the Me protons of **1** in the presence of **4** are summaried in Table 2. In all cases except **1e**, an equimolar amount of **4** is enough for an effective splitting of the Me proton signal. When twice molar amounts of **4** are used, the splitting is about doubled (Table 2). Previously, we have already reported as a preliminary communication that the **2** and **4** are effective as a chiral shift reagent for amines, alcohols, sulfoxides, selenoxides, phosphine oxides, phosphates, and arsine oxides.[5] We have also reported that **2** and **4** are useful as a chiral reagent to determine the absolute configuration of chiral compounds by ^{1}H NMR spectroscopy.[6]

Finally, we succeeded in the isolation of optically active arsine oxide as an inclusion complex with **2**. This inclusion complex is useful to store the optically active arsine oxide stably. The inclusion complex might also be useful to an enantioselective reaction of the optically active arsine oxide, namely, direct action of a reagent on the inclusion complex gives optically active arsine derivative.

Experimental

Material. Dialkylarylarsine oxides (**1**) were prepared according to the reported procedure.[7]

General Procedure of the Optical Resolution. For example, when a solution of racemic **1d** (0.12 g, 0.5 mmol) and **2** (0.14 g, 0.5 mmol) in benzene–hexane (1:1, 10 ml) was kept at room temperature for 5 h, a 1:1 inclusion compound (**3d**) of (+)-**1d** and **2** was obtained as colorless prisms (0.17 g, 64% yield, mp 167—168 °C), the optical purity of the (+)-**1d** and **3d** was determined to be 64% ee by the ^{1}H NMR spectroscopy as described in the following section. By the same procedure, racemic **1a**, **1b**, and **1e**—**h** were resolved (Table 1).

Determination of Optical Purity. For example, when the ^{1}H NMR spectrum of the 1:1 complex of (+)-**1d** and **2** (**3d**) in $CDCl_3$ in the presence of an equimolar amount of **4** by JEOR JNM-PMX 60 Spectrometer, the originally singlet Me signal of **1d** at δ=1.917 ppm splitted into the two signals at δ=1.750 and 1.783 ppm of 82:18 ratio, from the data the optical purity of the (+)-**1d** was determined to be 64% ee. When the spectrum was measured in the presence of two molar amounts of **4**, the signal of Me protons of (+)-**1d** appeared at δ=1.667 and 1.717 ppm. By this method, optical purity of (+)-**1b** and (+)-**1e**—**h** was determined (Tables 1 and 2), although the optical purity of (+)-**1a** was not determined because of an insolubility of **3a** in $CDCl_3$.

We wish to thank for the Ministry of Education, Science and Culture, for Grant-in-Aid for Developmental Scientific Research, No. 63840017.

References

1) L. Horner and H. Winker, *Tetrahedron Lett.*, **1964**, 3271.

2) F. Toda, *Top. Curr. Chem.*, **140**, 43 (1987); K. Tanaka and F. Toda, *Nippon Kagaku Kaishi*, **1988**, 1643.

3) F. Toda, K. Tanaka, and S. Nagamatsu, *Tetrahedron Lett.*, **25**, 4929 (1984); F. Toda, K. Tanaka, and T. C. W. Mak, *Chem. Lett.*, **1984**, 2085; F. Toda and K. Tanaka, *J. Org. Chem.*, **53**, 3607 (1988).

4) F. Toda, K. Tanaka, T. Omata, K. Nakamura, and T. Ōshima, *J. Am. Chem. Soc.*, **105**, 5151 (1983).

5) F. Toda, K. Mori, J. Okada, M. Node, A. Itoh, K. Oomine, and K. Fuji, *Chem. Lett.*, **1988**, 131.

6) F. Toda, K. Mori, and A. Satō, *Bull. Chem. Soc. Jpn.*, **61**, 4167 (1988).

7) G. Kamai, *Ber.*, **66**, 1779 (1933); G. J. Burrows, *J. Proc. R. Soc. N. S. W.*, **68**, 72 (1935).