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ASYMMETRIC OXIDATION REACTION OF THERMALLY DECOMPOSED PRODUCTS OF *meso*-1,1'-DIPHENYL-1,1'-AZODIETHANE

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meso-1,1'-Diphenyl-1,1'-azodiethane was thermally decomposed in the presence of the cobalt complex having an asymmetric ligand in benzene at 102°C *in vacuo*. The resulting reaction mixture reacted readily with oxygen to form products such as acetophenone and 1-phenylethanol, the latter being optically active.

In our previous paper$^{1)}$, we reported that organic radicals from 2,2',3,3'-tetramethyl-2,2'-azodibutyronitrile were stabilized by some metal complexes, particularly cobalt complexes such as $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II) [Co(II)TPP]. When the cobalt complex has an optically active ligand, the radicals located at the central cobalt will be stabilized stereoselectively. Therefore, the radicals may undergo a stereoselective oxidation on reacting with oxygen.

We have now confirmed the formation of an optically active 1-phenylethanol by bubbling oxygen into a reaction system, in which *meso*-1,1'-diphenyl-1,1'-azodiethane(referred to as *meso*-azo compound) had preliminarily been subjected to thermolysis in the presence of N,N'-disalicylidene-(1*R*,2*R*)-1,2-cyclohexanediiminatocobalt(II)(referred to as Co(II)(sal)$_2$(*R*-CHXDA))$^{2)}$ as an asymmetric complex.

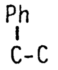
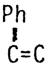
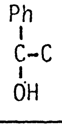
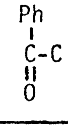
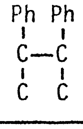
A benzene solution of *meso*-azo compound and a cobalt complex(Co(II)(sal)$_2$(*R*-CHXDA) or Co(II)TPP) was charged into an ampoule and degassed twice by means of a freeze-thaw method to remove oxygen. The ampoule was sealed *in vacuo*, and was allowed to stand in an oil bath at 102°C for 2 days. Thereafter, oxygen was bubbled into the reaction mixture at room temperature. After the oxidation, benzene was removed by freeze-drying method from the reaction mixture. The remainder was separated into hydrocarbons(contained ethylbenzene, styrene, and 2,3-diphenylbutane) and a mixture of the cobalt complex and oxidation products (acetophenone and 1-phenylethanol) by column chromatography(hexane-silica gel). The latter was silylated using trimethylsilyl chloride, and was separated into the silylated 1-phenylethanol and the mixture of cobalt complex and acetophenone in the same manner as described above. The optical rotation were measured with the silylated 1-phenylethanol. Quantitative analyses of the products were carried out with glc, ir, and nmr.

The specific rotation, $[\alpha]_D$, of an authentic sample of the silylated *S*-(-)-1-phenylethanol was determined as -49.5°(c=0.965), -48.9°(c=1.97), and -48.9° (c=3.93) at 21°C in benzene. ir : 1250cm^{-1}(-Si-C-), 841cm^{-1}(-Si-C-), 757cm^{-1} (-Si-C-), 1035cm^{-1}(-Si-O-C-) nmr : 0ppm(Si-CH_3 and TMS), 2.35ppm(α-methyl), 5.78ppm(α-hydrogen), 8.20ppm(phenyl) in $CDCl_3$. ($[\alpha]_D$ of *S*-(-)-1-phenylethanol$^{3)}$ before silylation : -48.2°(c=0.568), -45.2°(c=1.14), -44.4°(c=2.27) at 21°C in benzene.)

Table 1 shows the yields of oxidation products and specific rotation of the silylated 1-phenylethanol. The main product from the reaction without cobalt complex (run 1: control) was 2,3-diphenylbutane, no oxidation products being obtained. It is noted that a cobalt complex is necessary for the formation of oxidation products as seen in runs 2-8. In these runs, a drastic decrease is seen in the yield of 2,3-diphenylbutane.

On the oxidation of the reaction mixture, which had been obtained by the thermolysis of *meso*-azo compound in the presence of Co(II)$(sal)_2$(*R*-CHXDA), an optically active 1-phenylethanol was obtained (runs 2-4). *S*-(-)-1-Phenylethanol was also obtained from a reaction mixture, which had been obtained by the thermolysis of *meso*-azo compound in the presence of Co(II)TPP, followed by oxidation with oxygen in the presence of Co(II)$(sal)_2$(*R*-CHXDA) as the second cobalt complex(runs 6,7 and 8). These results are explained as the consequence of the formation of 1-phenylethyl radical in the oxidation stage from PhCH(CH_3)-NH-N=C(CH_3)Ph, which is produced in decomposition stage and is easily oxidized with the aid of the cobalt complexes.$^{5)}$ 1-Phenylethyl radicals should be stabilized stereoselectively through a bonding onto Co(II)$(sal)_2$(*R*-CHXDA) as reported in the previous paper.$^{1)}$ Oxygen molecules are considered to be inserted into the bond between 1-phenylethyl radical and cobalt.$^{6)}$ The stereoselection in the oxidation stage should be a consequence of the stereoselective stabilization of the radicals that was caused by the chiral circumstance around the central cobalt.

Table 1 Reaction Products and Optical Data of 1-phenylethanol

run	*meso*-azo compd. ($\times 10^2$ M)	metal complex added ($\times 10^3$ M)		Products(%)					$[\alpha]_D$ of silylated product from 1-phenylethanol obtained
		in decomp. stage	in oxidation stage	 $\overset{Ph}{C}-C$	 $\overset{Ph}{C}=C$	 $\underset{OH}{\overset{Ph}{C}}-C$	 $\underset{O}{\overset{Ph}{C}}-C$	 $\underset{C}{\overset{Ph}{C}}-\underset{C}{\overset{Ph}{C}}$	
0	4.25	0	0	1.6	0.4	0	0	95.0	——
1	4.25	0	[Co*]5.28	1.6	0.4	0	0	96.2	——
2	4.24	[Co*]4.94	0	0.7	1.4	8.0	61.0	11.7	-5.1(c=1.58)
3	3.30	[Co*]6.15	0	1.6	1.6	3.8	41.8	30.2	-0.4(c=0.82)
4	4.28	[Co*]5.21	0	1.4	2.3	7.8	57.4	24.5	-2.1(c=0.99)
5	4.19	CoTPP 6.91	0	0.2	2.1	10.0	61.9	7.9	0(c=2.50)
6	4.19	CoTPP 6.91	[Co*]5.28	0.6	2.7	10.6	67.0	7.4	-1.6(c=0.49)
7	4.22	CoTPP 6.85	[Co*]5.28	0.4	2.7	15.3	63.5	8.9	-1.6(c=0.44)
8	4.22	CoTPP 6.64	[Co*]3.43	0.4	2.7	8.6	61.1	9.8	-1.2(c=2.35)

[Co*] = Co(II)$(sal)_2$(*R*-CHXDA)

Decomposition Reaction Conditions: at 102°C in benzene for 2 days

Oxidation Reaction Conditions: bubbling oxygen at room temperature for 5 min. with Co(II)TPP, and for 10-20 min. with Co(II)$(sal)_2$(*R*-CHXDA).

No oxidation reaction took place when hydroquinone as a radical scavenger was added, prior to the oxidation after the decomposition stage.

This is the first report that deals with the oxidation of an optically inactive *meso*-compound with molecular oxygen giving an optically active product. A previous report[4)] by Howard et al. dealt with the stereospecific autoxidation of an optically active 1-bromo-2-methylbutane to an optically active 1-bromo-2-hydroxy-2-methylbutane.

References

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