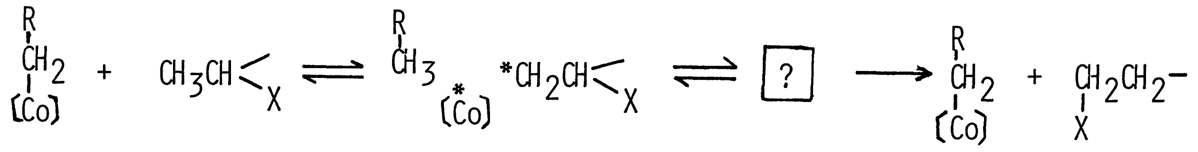
CHEMISTRY LETTERS, pp. 1135-1138, 1978. Published by the Chemical Society of Japan

PHOTOLYSIS AND THERMOLYSIS OF 2,2-DIPHENYL-2-HYDROXYETHYL-BIS(DIMETHYLGLYOXIMATO)PYRIDINE-COBALT(III), 2,2-DIPHENYL-2-HYDROXYETHYL COBALOXIME

Masaru TADA*, Masami OKABE, and Kyo MIURA
Department of Chemistry, School of Science and Engineering,
Waseda University, Shinjuku, Tokyo 160

Photolysis of 2,2-diphenyl-2-hydroxyethyl cobaloxime in the absence of oxygen gave deoxybenzoin, with phenyl rearrangement, and 1,1-diphenylethanol, with hydrogen abstraction, in various solvents. Thermolysis gave the similar results but the formation of 1,1-diphenylethylene becomes a major process.

5'-Deoxyadenosylcobalamin (coenzyme B_{12}) is an important cofactor for diol-dehydrase or methylmalonyl-CoA mutase, which causes the isomerization of propan-1,2-diol into propan-1,1-diol (propanal equivalent) or methylmalonyl-CoA into succinyl-CoA, and similar types of transformation of substrates. The major role of coenzyme B_{12} in these enzyme reactions is still in the black box as illustrated in eq. 1, but it is generally believed that coenzyme B_{12} is involved in the deep sites of these transformations.$^{1-4)}$



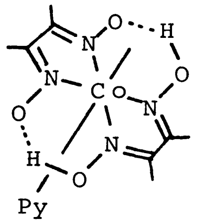
--- eq. 1.

[Co]-CH_2R: 5'-DEOXYADENOSYLCOBALAMIN * IONIC OR RADICAL SPECIES

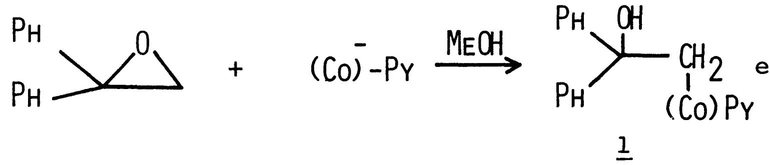
X : OH, NH_2, CO-SCoA, $CH_2(NH_2)COOH$, $CH_2(=CH_2)COOH$

In the line of our study on the model compound of coenzyme B_{12},$^{5,6)}$ we have explored the chemical properties of 2,2-diphenyl-2-hydroxyethyl-bis(dimethylglyoximato)pyridinecobalt(III) (1) (cobaloxime 1 hereafter), in which the migration of phenyl group can be expected. We selected the cobaloxime (1) as the substrate of a model reaction for the future test of the electronic effect of a migrating group, and carried out the photochemical and thermal decomposition of cobaloxime (1).

Cobaloxime (1) was prepared by the reaction of 2,2-diphenyloxirane with the cobaloxime anion prepared *in situ* from the ligands, cobalt(II) chloride, and sodium borohydride (eq. 2).[7] The structure of cobaloxime (1) was ascertained by elemental analysis and spectral data. Irradiation (60w fluorescent lamp) of the solution of cobaloxime (1) gave deoxybenzoin (2) and 1,1-diphenylethanol (3), whereas irradiation of the solution bubbled by oxygen gave 2,2-diphenyl-2-hydroxyethanal (4) and benzophenone (5). The photo-products from the deoxygenated solution were only 2 and 3 beside the persisted cobaloxime (1), and the combined yield of 2 and 3 was almost quantitative based on the consumed cobaloxime (1).



: (Co)Py



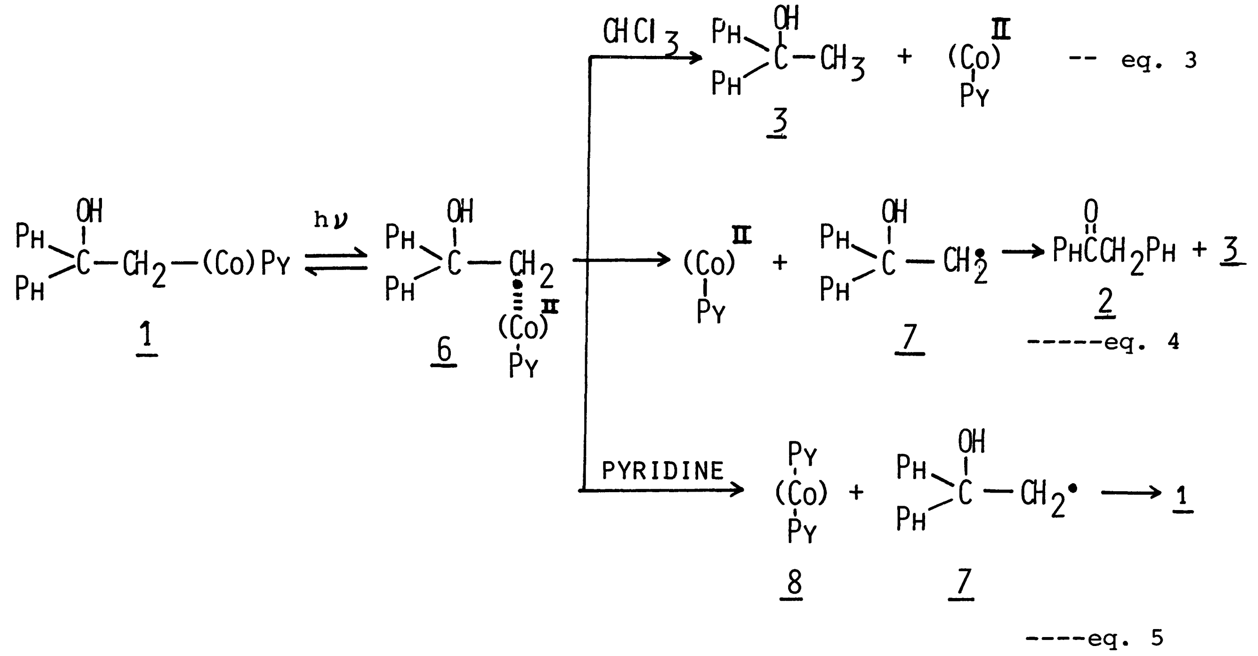
eq. 2.

Solvent effect on the relative rate of the disappearance of 1 and the composition of the products mixture are listed in the table 1. The composition of the products can be understood as a reflection of the hydrogen donating ability of the solvent as exemplified by the cases of chloroform, 2:3 = 5:95, and benzene, 2:3 = 100:0. Apparently the relative rate of consumption of cobaloxime (1) does not depend on the polarity of solvent and the prominent rate in chloroform and pyridine must be due to the hydrogen donating ability of chloroform [8] and the coordination ability of pyridine. The solvent effect and the formation of 1,1-diphenylethanol show the photolysis of the carbon-cobalt bond takes a homolytic process giving a radical intermediate (7) which collapses into 2 by phenyl migration followed by hydrogen loss and into 3 by a direct hydrogen abstraction. Though we can not specify the existence of cobalt catalysis for the phenyl migration, a radical (6) formed immediately after photolysis must be still in the coordination sphere of cobalt and has two competitive processes, one is a recombination to give the starting

Table 1. Photolysis of cobaloxime (1).[a,b]

Solvent	$k_{rel.}$	Composition of products 2(%)	 3(%)
Chloroform	12	5	95
Dichloromethane	1.4	72	28
Propionitrile	1.3	65	35
Acetonitrile	1.2	88	12
Benzene	1.2	100	0
Chlorobenzene	1.0	100	0
Pyridine	ca. 8	100	0

a) 1: $3X10^{-3}$mol/l. b) Irradiation for 16 h under water cooling cobaloxime (1) and another is the escape of 1,1-diphenylethanol-2-yl radical (7) which collapse into 2 and 3. The paired radical (6) can abstract a hydrogen from the solvent cage to give 3 and cobaloxime radical. In the same manner the paired radical (6) can be coordinated by pyridine to give bis-pyridinecobaloxime (8) and the free radical (7). These properties must be the origin of the enhanced reaction rate of 1 in chloroform, a strong hydrogen donating solvent, and in pyridine, a strong ligand to cobalt(II) (eq. 3-5).



Thermal decomposition of cobaloxime (1) was carried out by heating the solution of 1 in an oil bath. The thermolysis gave deoxybenzoin (2), 1,1-diphenylethanol (3), and 1,1-diphenylethylene (9). Cobaloxime(1) gives 9 as a major product in the most cases and this process may be regarded as ionic elimination reaction,[9)] but the formation of 2 and 3 in xylene, a hydrogen donating solvent, shows the homolytic nature of the thermolysis.

There are several different features between photolysis and thermolysis. The formation of 1,1-diphenylethylene (9) on thermolysis as a major product is in sharp contrast with the photolysis in which no 9 was formed. Pyridine retards the thermolysis rate whereas it accelerates the photolysis rate. The effect of pyridine reveals the more or less different nature of the intermediate formed on thermolysis and photolysis. We consider that the difference must originate by the innitial removal of axially coordinated pyridine giving the intermediate(10) which give 7 on further thermolysis (eq. 6). The thermolysis in pyridine, therefore, must favor the backward coordination of pyridine to regenerate the cobaloxime (1).

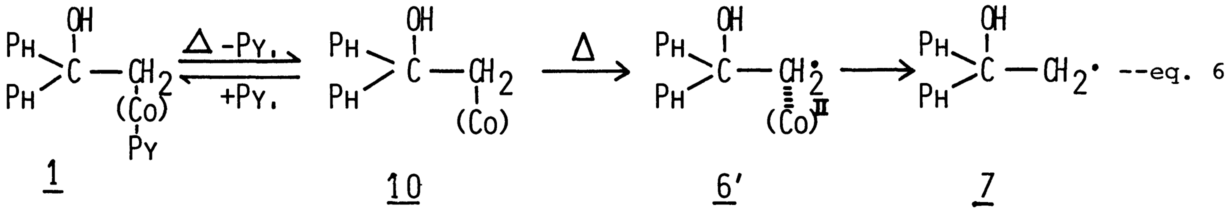


Table 2. Thermolysis of cobaloxime (1).

Solvent	Temperature (°C)	time (hr)	Conversion (%)	Composition (%) 2	3	9
Xylene	137[a)]	1	100	12	-	88
Xylene	95-107[b)]	24	100	16	9	75
Chlorobenzene	95-107[b)]	24	100	10	-	90
Chlorobenzene	80-90[b)]	24	100	12	-	88
Pyridine	95-107[b)]	24	ca. 40	62	-	38
Pyridine	80-90[b)]	24	ca. 20	20	-	80
Benzene	80[a)]	55	ca. 30	12	-	88
Acetonitrile	81[a)]	55	ca. 20	50	-	50

a) Refluxing temperature. b) Thermolyses at these temperature were carried out by heating two or more solutions at the same time in an oil bath.

The lack of 3 in the thermolysis of 1 in xylene (137°C) must be due to the dehydration of 3, a primary product, to give 9 under the reaction conditions. The favorable formation of 2 in the thermolyses in pyridine (95-107°C) and acetonitrile can not be well understood, but some polar nature of the homolytic rearrangement can be considered.

Though there are small differences in the nature between photolysis and thermolysis of cobaloxime (1), both processes give deoxybenzoin (2) by the homolytic fission of the carbon-cobalt bond. This feature, though the role of cobalt catalysis in the rearrangement step is not clear, must be a reasonable simulation of the coenzyme B_{12} assisted rearrangement of the substrates in enzymatic reactions.

References

1) R. H. Abeles, and D. Dolphin, Acc. Chem. Res., 9, 114 (1976).
2) G. N. Schrauzer, Angew. Chem. Int. Ed., 16, 233 (1977).
3) E. J. Corey, N. J. Cooper, and M. L. H. Green, Proc. Natl. Acad. Sci. U. S. A., 74, 811 (1977).
4) B. T. Golding, C. S. Sell, and P. J. Sellars, J. Chem. Soc., Chem. Commun., 1977, 693.
5) M. Tada and H. Ogawa, Tetrahedron Lett., 1973, 2639.
6) H. Shinozaki, H. Ogawa, and M. Tada, Bull. Chem. Soc. Jpn., 49, 775 (1976).
7) F. R. Jensen, V. Madan, and D. H. Buchanan, J. Amer. Chem. Soc., 92, 1414 (1970).
8) J. K. Kochi, Ed., "Free Radicals", John-wiley and Sons, vol.1, New York, (1973), p. 303.
9) R. B. Silverman and D. Dolphin, J. Amer. Chem. Soc., 98, 4626 (1976).

(Received July 24, 1978)