Aryl Rearrangement on the Photolysis of 2-Aryl-2-ethoxy-2-phenylethyl Cobaloxime

Masaru TADA,* Kunimi INOUE, and Masami OKABE

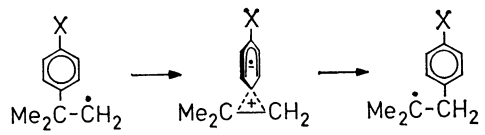
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 160

(Received June 7, 1982)

The photolysis of 2-aryl-2-ethoxy-2-phenylethyl cobaloxime followed by hydrolysis gave two kinds of substituted 1,2-diphenylethanones arising *via* phenyl or substituted-phenyl migration. The substituent effect on the aryl rearrangement is similar to that on the reported neophyl rearrangement, and the rearrangement takes place by a radical mechanism without the deep involvement of cobaloxime(II).

Organo-bis(dimethylglyoximato)(pyridine)cobalt(III), hereafter organo-cobaloxime(III) or R–(Co), has been often used as a model compound of coenzyme B_{12}, organo-cobalamin(III).[1] The photolysis of the Co–C bond of an organo-cobaloxime(III) gives organic radical and cobaloxime(II), (Co^{II}), pair[2] which reasonably mimics the substrate radical and cobalamin(II) in an enzymatic system.[3] In studies on the photolyses of β-acylalkyl cobaloximes, we have demonstrated that the migration of the β-acyl group takes place in a radical state.[1b] However, we have not ruled out the possibility that the rearrangement takes place under the influence of the paramagnetic cobaloxime(II). Some interactions between cobaloxime(II) and the organic radical can be envisaged; one is a charge transfer, and another is a orbital interaction.

It has been established that the neophyl rearrangement has a slightly polar character as depicted in Eq. 1 in an exaggerated manner.[4] These situations

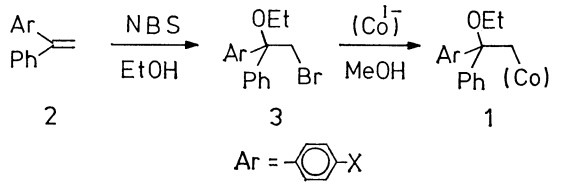


(1)

prompted us to investigate the substituent effect in the aryl rearrangement on the photolysis of 2-aryl-2-ethoxy-2-phenylethyl cobaloxime(III) (**1**). The same substituent effect as the reported neophyl rearrangement should be observed if the rearrangement is not influenced by cobaloxime(II).

Results

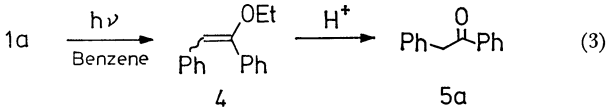
Preparation of 2-Aryl-2-ethoxy-2-phenylethyl Cobaloxime (1). The route of synthesizing the organo-cobaloxime is shown in Eq. 2. 1-Aryl-1-phenylethene



(2)

(**2**) was obtained by the reaction of (*p*-substituted phenyl)magnesium bromide with acetophenone or the reaction of phenylmagnesium bromide with *p*-substituted acetophenone followed by dehydration. The olefin **2** was then treated with *N*-bromosuccinimide in ethanol to give 2-aryl-2-ethoxy-2-phenylethyl bromide (**3**). The organo-cobaloxime **1** was prepared by the reaction of the bromide **3** with cobaloxime(I) anion.[5] The structure of the organo-cobaloxime **1** was ascertained by elemental analysis and spectral data (see the Experimental part).

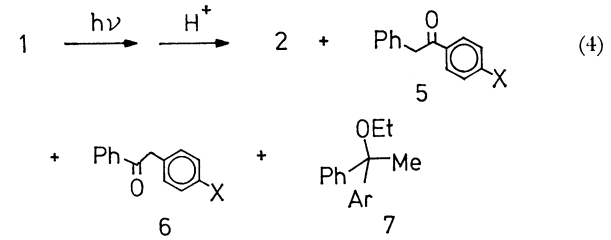
Photolysis of Organo-cobaloxime 1 in Benzene. Anaerobic photolysis followed by acid treatment of 2,2-diphenyl-2-ethoxyethyl cobaloxime (**1a**) gave 1,2-diphenylethanone (**5a**), which formed by the hydrolysis of the primary products, *cis*- and *trans*-enol ethers **4**[6] (Eq. 3). The photolyses of the organo-cobaloximes



(3)

1b—**e** followed by hydrolyses gave two kinds of substituted 1,2-diphenylethanones arising *via* phenyl group migration (**5b**—**d**) or *via* substituted phenyl group migration (**6b**—**e**) (Table 1). The residual organo-cobaloximes decomposed into olefins **2** on chromatography of the products on Florisil in the workup step. This property is common to 2-alkoxy-2,2-diarylethyl cobaloximes.[7] The material balance before and after the reaction is well maintained in all photolyses.

When the *p*-substituent X was an electron-withdrawing group, the substituted phenyl group migrated in preference to the phenyl group. When the substituent was cyano group (X=CN), no migration of phenyl group was observed. When the substituent was an electron-releasing group (X=Me), the phenyl group migrated preferentially.



(4)

Photolysis of Organo-cobaloxime 1 in Chloroform or Acetonitrile. The anaerobic photolysis of **1** in chloroform gave the ketones **5** and **6** together with 1-aryl-1-ethoxy-1-phenylethane (**7**) (Table 2).[8] The latter product is expected to be generated by the hydrogen abstraction of the radical intermediate from chloroform. The photolysis in chloroform is faster than in benzene and no starting material was left under similar

Table 1. Photolysis of organo-cobaloxime **1** in benzene

Substrate	Substituent X	Product composition (%) 5	6	Ratio 6/5	k_{rel}[a]	Total yield/% 5+6
1a	H	50[b]	50[b]	1.00	1.00	62
1b	Me	60	40	0.67	0.72	73
1c	Cl	24	76	3.17	1.76	78
1d	Br	21	79	3.76	1.91	93
1e	CN	0	100	—	35.0	75

a) Relative rate of the migration of *p*-substituted phenyl group to that of the phenyl group; the values were determined by the thermal decomposition of the ester of 3-aryl-3-methylperoxybutanoic acid (C. Rüchardt and R. Hecht).[4] b) In the case of **1a** the product was divided equally been **5** and **6**.

Table 2. Photolysis of organo-cobaloxime **1** in chloroform or acetonitrile

Substrate	Substituent X	Solvent	Product composition (%) 5	6	7	Product ratio 6/5	7/5	Total yield/% 5+6+7
1a	H	$CHCl_3$	27[a]	27[a]	46	1.00	1.69	82
1b	Me	$CHCl_3$	28	16	56	0.57	2.00	70
1c	Cl	$CHCl_3$	17	50	33	2.94	1.92	82
1e	CN	$CHCl_3$	0	100	0	—	—	72
1b	Me	MeCN	59	41	Trace	0.69	*ca.* 0	58
1c	Cl	MeCN	21	79	0	3.76	0	80
1e	CN	MeCN	0	100	0	—	—	73

a) In the case of **1a** the migrated product was divided equally between **5** and **6**.

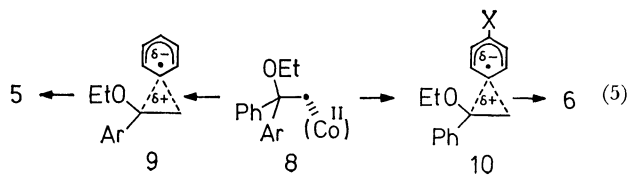
conditions to the photolysis in benzene. The photolyses of the cobaloxime in chloroform or chloroform itself is expected to produce hydrogen chloride in trace amount, and the acid hydrolysis of the enol ethers seem to take place under the photolysing conditions.

The ratios of **6/5** in chloroform are similar to those in benzene. The ratio of hydrogen abstraction to phenyl rearrangement (**7/5**) does not vary much with the substituent X on the non-rearranged aryl group.

The photolysis of organo-cobaloxime **1** in acetonitrile, a polar solvent, gave similar results as in benzene except for the formation of **7b** in trace amount from **1b** (Table 2).

Discussion

In the present study we found that the order of the aryl groups in migration-ability is similar to the order in the neophyl rearrangement by a radical mechanism.[4] This finding indicates that the aryl migration on the photolysis of organo-cobaloxime **1** involves a radical mechanism. The substituent effect observed in the present study and the reported neophyl rearrangement is interpreted in terms of the slightly polar transition state (**9** or **10**). The polarization can be ascribed to the electron-releasing character of the



cyclopropane ring.[9] When the substituent X is an electron-withdrawing group, the transition state **10** is more stabilized and the migration of the *p*-substituted phenyl group becomes more favorable (Eq. 5).

The ratio of **6/5** is not much affected by the polarity of the solvent; this indicates that the charge transfer or electron transfer between (Co^{II}) and the radical species is not an important factor in driving the rearrangement. Furthermore the charge separation in the transition states (**9** and **10**) is not so extensive that the stabilization of the transition states does not depend strongly on the polarity of the solvent. From the limitation of the present study we can not discuss the absolute formation rate of **5** and **6**, and the discussion must be limited to the relative rate of phenyl or aryl migration. The present findings are explained by the assumption that both transition states **9** and **10** are stabilized to a similar extent by a polar solvent. The solvent dependence of the formation of **7** can be understood as a consequence of the hydrogen donating ability of the solvent.[10] It can be assumed that the rates of hydrogen abstraction and phenyl migration are independent of the substituent X on the non-rearranged aryl group. Therefore the variation in the formation of **5** and **7** depending on X in chloroform can be explained in terms of the difference in the rate of the migration of the substituted phenyl group.

The organo-cobaloxime **1e** (X=CN) did not give the hydrogen-abstracted product **7** even in chloroform, a strong hydrogen donor. On the other hand, the decomposition of the ester of 3-(*p*-cyanophenyl)-3-methylperoxybutanoic acid gives a small amount of the hydrogen-abstracted product even in tetralin,[4] which is a weaker hydrogen donor than chloroform.[10] It

is considered that cobaloxime(II) in the radical pair **8** may promote the rearrangement by weak orbital interaction.

In conclusion the photolysis of organo-cobaloxime **1** causes the homolytic cleavage of Co–C bond, and the resulting radical pair does not cause the charge transfer or electron transfer between cobaloxime(II) and the organic radical. The intervention of ionic species in the rearrangement is thus ruled out, though the weak orbital interaction in the radical pair may promote the rearrangement. The explanation of the insensitivity of the formation ratio **6**/**5** to solvent polarity must await more ellaborate studies.

Experimental

Preparation of 1-Aryl-1-phenylethene (2). The preparations of 1,1-diphenylethene (**2a**),[11] 1-(*p*-methylphenyl)-1-phenylethene (**2b**),[12] 1-(*p*-chlorophenyl)-1-phenylethene (**2c**),[13] and 1-(*p*-bromophenyl)-1-phenylethene (**2d**),[14] are described in the literature. 1-(*p*-Cyanophenyl)-1-phenylethene (**2e**) is prepared as described below.

To a solution of *p*-cyanoacetophenone (7.25 g, 50 mmol) in dry ether (100 cm^3) a solution of phenylmagnesium bromide (50 mmol) in dry ether (20 cm^3) was added dropwise at 0 °C. After stirring for 30 min at room temperature, saturated ammonium chloride solution (10 cm^3) was added dropwise at 0 °C. The ethereal solution was decanted and evaporated to give crude 1-(*p*-cyanophenyl)-1-phenylethanol. A mixture of the crude material and powdered potassium hydrogensulfate (8 g) in toluene (50 cm^3) was refluxed for 10 h. After the addition of water (50 cm^3), the mixture was extracted with ether (2×50 cm^3). The combined ethereal extracts were dried over anhydrous sodium sulfate. Distillation gave 5.06 g (49%) of pure **2e**, bp 116 °C/93 Pa. Found: C, 87.52; H, 5.58; N, 6.49%. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82%. IR (CCl_4) 2225, 901, and 698 cm^{-1}; NMR (CCl_4) δ=5.51 (d, 1H, J=1 Hz), 5.57 (d, 1H, J=1 Hz), 7.22—7.45 (m, 5H), 7.47 (d, 2H, J=8 Hz), and 7.63 (d, 2H, J=8 Hz).

Preparation of 2-Aryl-2-ethoxy-2-phenylethyl Bromide (3). 2,2-Diphenyl-2-ethoxyethyl bromide (**3a**) was prepared from **2a** by the reported method.[15] The general procedure for the preparations of 2-ethoxy-2-(*p*-methylphenyl)-2-phenylethyl bromide (**3b**), 2-(*p*-chlorophenyl)-2-ethoxy-2-phenylethyl bromide (**3c**), 2-(*p*-bromophenyl)-2-ethoxy-2-phenylethyl bromide (**3d**), and 2-(*p*-cyanophenyl)-2-ethoxy-2-phenylethyl bromide (**3e**) is described below.

To a suspension of *N*-bromosuccinimide (2 g, 11.2 mmol) in dry ethanol (20 cm^3) a solution of **2** (10 mmol) in dry ethanol (10 cm^3) was added dropwise at −10 °C. After stirring for 2 h at −10 °C and for 4 h at room temperature, the resulting succinimide was filtered off and the filtrate was evaporated. The residue was placed on a silica gel column and eluted with benzene to give the bromide **3** (53—77%). **3b—e** were converted directly to the organo-cobaloximes **1b—e** without further purification.

3b, oil; NMR (CCl_4) δ=1.18 (t, 3H, J=7 Hz), 2.25 (s, 3H), 3.23 (q, 2H, J=7 Hz), 4.13 (s, 2H), and 6.95—7.48 (m, 9H).

3c, oil; NMR (CCl_4) δ=1.23 (t, 3H, J=7 Hz), 3.23 (q, 1H, J=7 Hz), 3.27 (q, 1H, J=7 Hz), 4.05 (d, 1H, J=12 Hz), 4.13 (d, 1H, J=12 Hz), and 7.08—7.43 (m, 9H).

3d, oil; NMR (CCl_4) δ=1.20 (t, 3H, J=7 Hz), 3.18 (q, 1H, J=7 Hz), 3.23 (q, 1H, J=7 Hz), 4.07 (d, 1H, J=12 Hz), 4.13 (d, 1H, J=12 Hz), and 7.06—7.58 (m, 9H).

3e, mp 97—99 °C; IR (CCl_4) 2225 and 697 cm^{-1}; NMR (CCl_4) δ=1.20 (t, 3H, J=7 Hz), 3.18 (q, 1H, J=7 Hz), 3.31 (q, 1H, J=7 Hz), 4.12 (d, 1H, J=10 Hz), 4.23 (d, 1H, J=10 Hz), 7.12—7.40 (m, 5H), and 7.45 (bs, 4H).

Preparation of 2-Aryl-2-ethoxy-2-phenylethyl Cobaloxime (1). The organo-cobaloxime **1** was prepared from the bromide **3** (5 mmol) and cobaloxime(I) (6 mmol) in methanol (15 cm^3) in the conventional manner.[7] Chromatography on aluminum oxide containing 10% (w/w) of water using benzene–chloroform as an eluent and recrystallization from acetonitrile yielded pure **1** (44—65%).

The strong infrared absorption bands due to the cobaloxime(III) moiety are common to all **1**: 1560, 1450, 1240—1200, and 1100—960 cm^{-1}.

1a, mp 142 °C (decomp). Found: C, 58.29; H, 5.96; N, 11.99%. Calcd for $C_{29}H_{36}N_5O_5Co$: C, 58.68; H, 6.11; N, 11.80%. NMR ($CDCl_3$) δ=1.22 (t, 3H, J=7 Hz), 1.83 (s, 12H), 2.56 (s, 2H), 3.00 (q, 2H, J=7 Hz), 6.85—7.30 (m, 12H), 7.45—7.63 (m, 1H), and 8.35—8.47 (m, 2H).

1b, mp 146 °C (decomp). Found: C, 59.30; H, 6.51; N, 11.68%. Calcd for $C_{30}H_{38}N_5O_5Co$: C, 59.30; H, 6.30; N, 11.53%. NMR ($CDCl_3$) δ=1.29 (t, 3H, J=7 Hz), 1.81 (s, 12H), 2.15 (s, 3H), 2.45 (d, 1H, J=10 Hz), 2.65 (d, 1H, J=10 Hz), 2.97 (q, 2H, J=7 Hz), 6.73—7.27 (m, 11H), 7.39—7.60 (m, 1H), and 8.32—8.45 (m, 2H).

1c, mp 156 °C (decomp). Found: C, 55.73; H, 5.75; N, 11.26%. Calcd for $C_{29}H_{35}N_5O_5ClCo$: C, 55.46; H, 5.62; N, 11.15%. NMR ($CDCl_3$) δ=1.20 (t, 3H, J=7 Hz), 1.82 (s, 12H), 2.36 (d, 1H, J=10 Hz), 2.56 (d, 1H, J=10 Hz), 2.96 (q, 1H, J=7 Hz), 2.99 (q, 1H, J=7 Hz), 6.78—7.37 (m, 11H), 7.43—7.56 (m, 1H), and 8.36—8.55 (m, 2H).

1d, mp 158 °C (decomp). Found: C, 52.10; H, 5.16; N, 10.08%. Calcd for $C_{29}H_{35}N_5O_5BrCo$: C, 51.80; H, 5.25; N, 10.41%. NMR ($CDCl_3$) δ=1.24 (t, 3H, J=7 Hz), 1.85 (s, 12H), 2.35 (d, 1H, J=10 Hz), 2.64 (d, 1H, J=10 Hz), 2.97 (q, 1H, J=7 Hz), 3.03 (q, 1H, J=7 Hz), 6.94—7.38 (m, 11H), 7.51—7.71 (m, 1H), and 8.46—8.56 (m, 2H).

1e, mp 154 °C (decomp). Found: C, 58.03; H, 5.78; N, 13.80%. Calcd for $C_{30}H_{35}N_6O_5Co$: C, 58.25; H, 5.70; N, 13.59%. NMR ($CDCl_3$) δ=1.22 (t, 3H, J=7 Hz), 1.87 (s, 6H), 1.91 (s, 6H), 2.43 (d, 1H, J=10 Hz), 2.63 (d, 1H, J=10 Hz), 3.03 (q, 1H, J=7 Hz), 3.10 (q, 1H, J=7 Hz), 6.98—7.87 (m, 12H), and 8.43—8.62 (m, 2H). IR ($CHCl_3$) 2230 cm^{-1}.

Photolysis of Organo-cobaloxime 1. A Typical Procedure for 1a in Benzene: A solution of the organo-cobaloxime **1a** (1.25×10^{-3} mol dm^{-3}) in benzene (15 cm^3) was placed in a Pyrex tube, dipped in an ultrasonic bath, and bubbled with argon from a syringe needle for 30 min. The solution was irradiated externally for 12 h with a 450-W high-pressure Hg lamp mounted in a rotary irradiation apparatus (Rikosha RH-400), the distance between the lamp and the reaction tube being *ca.* 5 cm. The reaction solution was evaporated *in vacuo* and the residue was chromatographed on Florisil, using chloroform as an eluent, to give the mixture of *cis*- and *trans*-enol ethers **4**[16] containing a small amount of **2a**. A solution of the enol ethers **4** in ether/ methanol/ aqueous hydrogen chloride (6 mol dm^{-3}) (5:3:1) was stirred overnight. After the addition of saturated aqueous sodium hydrogencarbonate, the mixture was extracted several times with ether. The combined ethereal extracts were washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 1,2-diphenylethanone (**5a**) and **2a**.

Photolyses of ***1b—e*** *in Benzene*: The photolyses of **1b—e** were carried out by the procedure described above. A similar workup gave the mixture of olefin **2** and enol ethers containing a small amount of hydrolysis products **5** and **6**. Acid treatment of the mixture gave the products **2**, **5**, and **6**, which were identified by comparison with authentic samples synthesized by reported methods.[16-22] The results are summarized in Table 1. The physical data of the products are as follows.

5b,[16] mp 106—108 °C. IR ($CHCl_3$) 1677 cm^{-1}; NMR ($CDCl_3$) δ=2.38 (s, 3H), 4.23 (s, 2H), 7.03—7.43 (m, 7H), and 7.91 (d, 2H, J=8 Hz).

6b,[17] mp 92—94 °C. IR ($CHCl_3$) 1675 cm^{-1}; NMR ($CDCl_3$) δ=2.28 (s, 3H), 4.22 (s, 2H), 7.14 (s, 4H), 7.37—7.60 (m, 3H), and 7.87—8.17 (m, 2H).

5c,[18] mp 106—108 °C. IR ($CHCl_3$) 1680 cm^{-1}; NMR ($CDCl_3$) δ=4.22 (s, 2H), 7.22 (bs, 5H), 7.34 (d, 2H, J=8 Hz), and 7.90 (d, 2H, J=8 Hz).

6c,[19] mp 132—133 °C. IR ($CHCl_3$) 1681 cm^{-1}; NMR ($CDCl_3$) δ=4.22 (s, 2H), 7.03—7.62 (m, 7H), and 7.82—8.07 (m, 2H).

5d,[20] mp 110—111 °C. IR ($CHCl_3$) 1680 cm^{-1}; NMR ($CDCl_3$) δ=4.18 (s, 2H), 7.20 (bs, 5H), 7.48 (d, 2H, J=9 Hz), and 7.76 (d, 2H, J=9 Hz).

6d,[21] mp 145—147 °C. IR ($CHCl_3$) 1681 cm^{-1}; NMR ($CDCl_3$) δ=4.20 (s, 2H), 7.08 (d, 2H, J=9 Hz), 7.30—7.64 (m, 5H), and 7.88—8.01 (m, 2H).

6e,[22] mp 112—114 °C. IR ($CHCl_3$) 2240 and 1686 cm^{-1}; NMR ($CDCl_3$) δ=4.33 (s, 2H), 7.20—7.69 (m, 7H), and 7.84—8.12 (m, 2H).

Photolysis of ***1a*** *in Chloroform*: The same procedure for the photolysis in benzene was employed but the acid treatment was not required. The products thus obtained are **5a** and 1,1-diphenyl-1-ethoxyethane (**7a**) (see Table 2).

7a, oil. IR (CCl_4) 702 cm^{-1}; NMR (CCl_4) δ=1.27 (t, 3H, J=7 Hz), 1.78 (s, 3H), 3.20 (q, 2H, J=7 Hz), and 6.90—7.38 (m, 10H). The structure of **7a** was determined by an unequivocal synthesis from 1,1-diphenylethanol,[11] diethyl sulfate, and sodium hydride in THF.

Photolyses of ***1b***, ***1c***, *and* ***1e*** *in Chloroform*: The photolyses of **1b**, **1c**, and **1e** were carried out by using the same procedure as for the photolysis of **1a** in chloroform, and the results are summarized in Table 2.

7b, oil. IR (CCl_4) 701 cm^{-1}; NMR (CCl_4) δ=1.15 (t, 3H, J=7 Hz), 1.74 (s, 3H), 2.23 (s, 3H), 3.18 (q, 2H, J=7 Hz), and 6.79—7.28 (m, 9H). The structure of **7b** was determined by an unequivocal synthesis from 1-(*p*-methylphenyl)-1-phenylethanol,[12] diethyl sulfate, and sodium hydride in THF.

7c, oil. IR (CCl_4) 701 cm^{-1}; NMR (CCl_4) δ=1.16 (t, 3H, J=7 Hz), 1.74 (s, 3H), 3.18 (q, 2H, J=7 Hz), and 6.97—7.29 (m, 9H). The structure of **7c** was determined by an unequivocal synthesis from 1-(*p*-chlorophenyl)-1-phenylethanol,[13] diethyl sulfate, and sodium hydride in THF.

Photolyses of ***1b***, ***1c***, *and* ***1e*** *in Acetonitrile*: The same procedure described for the photolysis of **1a** in benzene was employed and the results are summarized in Table 2.

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