The Hydrogen-transfer Reaction of a Diazo Compound Catalyzed by a Cobalt Complex

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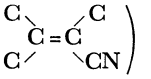
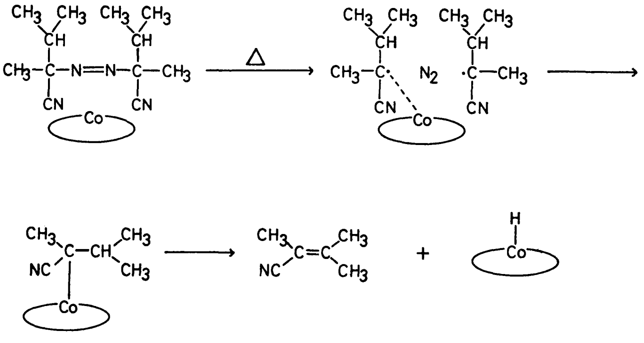
Acetophenone α-methylbenzylhydrazone was produced by the thermolysis of 1,1′-diphenylazoethane in the presence of a cobalt complex in benzene. In this reaction, the cobalt complex seemed to stabilize the radicals formed from the azo compound by the elimination of α-hydrogen. The stabilized radicals underwent 1,3-rearrangement to form acetophenone α-methylbenzylhydrazone. The driving force of this rearrangement is considered to be the nature of the cobalt atom, which prefers a bond formation with a more electronegative nitrogen atom to a carbon atom.

In our previous study,[1] it was found that scarcely no inner olefin  was produced by the thermolysis of 2,2′,3,3′-tetramethyl-2,2′-azodibutyronitrile in benzene, but the substance was produced in quantity in the presence of a cobalt complex such as Co(II)TPP. The mechanism for the formation of the inner olefin was explained by the following scheme:



Scheme 1.

where the participation of Co(II)TPP was assumed in a certain hydrogen-transfer reaction.

A typical example of a hydrogen-transfer reaction catalyzed by a metal complex is a reaction in the co-enzyme vitamin B_{12}. Particularly, 1,2-hydrogen transfer processes from glycol to aldehyde catalyzed by diol dehydrase were studied; the co-enzyme B_{12} was established as playing an important role in the hydrogen-transfer reaction.[2]

The present paper reports that acetophenone α-methylbenzylhydrazone is produced from 1,1′-diphenylazoethane by thermolysis in the presence of a cobalt complex as a result of a hydrogen-transfer reaction (1,3-rearrangement). This reaction provides not only evidence for a possible interaction between a transition-metal complex and a free radical, but also a model for the rearrangement reaction of vitamin B_{12}.

Experimental

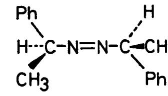
Syntheses of Azo Compounds. (*S*)-(−)-α-Methylbenzylamine and (*R*)-(+)-α-methylbenzylamine were obtained using the resolution method of Theilacker.[3]

The levorotatory amine: $\alpha_D^{23}=-38.2°$(neat) ($\alpha_D^{22}=-38.3°$).[3]

The dextrorotatory amine: $\alpha_D^{23}=+38.3°$(neat) ($\alpha_D^{22}=+37.16°$).[3]

(*S*,*S*)-(−)-1,1′-Diphenylazoethane (*SS*-Azo compound) was prepared according to the method of Green *et al.*[4]

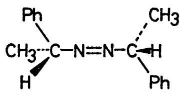
$[\alpha]_D^{18}=-284.2°$ (453.8 mg/5 ml CCl_4) ($[\alpha]_D^{25}=-304.9°$ (35.8 mg/2 ml CCl_4)).[4]



SS-Azo compound

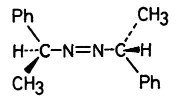
(*R*,*R*)-(+)-1,1′-Diphenylazoethane (*RR*-Azo compound) was prepared by means of the procedure used in the case of the *SS*-Azo compound except for the use of (*R*)-(+)-α-methylbenzylamine in place of (*S*)-(−)-α-methylbenzylamine.

$[\alpha]_D^{18}=+288.8°$(156.8 mg/5 ml CCl_4)



RR-Azo compound

meso-1,1′-Diphenylazoethane (*RS*-Azo compound) was prepared starting with racemic α-methylbenzylamine according to the procedure described above; when the reaction products (mixtures of *SS*, *RR*, and the *RS*-Azo compound) were allowed to stand in a refrigerator, crystals of the *RS*-Azo compound were formed. The crystals were recrystallized twice from ethanol; white prism crystals; mp 72.5—73.5 °C (72—73 °C).[4]



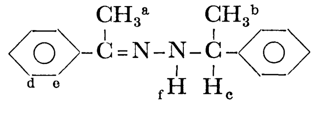
RS-Azo compound

Preparation of Metal Complexes. Tetraphenylporphyrin (H_2TPP) was prepared according to the method of Falk.[5] Cobalt(II) tetraphenylporphyrin [Co(II)TPP] was prepared according to the method of Rothemund and Menotti.[6] Ni(II)-TPP, Mn(II)TPP, and Cu(II)TPP were prepared using nickel(II) acetate, manganese(II) acetate, and copper(II) acetate, respectively, in place of cobalt(II) acetate.

(1*R*,2*R*)-*N*,*N*′-Disalicylidene-1,2-cyclohexanediaminatocobalt(II) [Co(II)$(sal)_2$(*R*-CHXDA)] was prepared according to the method of Aoi *et al.*[7] Ni(II)$(sal)_2$(*R*-CHXDA), Mn(II)-$(sal)_2$(*R*-CHXDA), and Cu(II)$(sal)_2$(*R*-CHXDA) were prepared using nickel(II) acetate, manganese(II) acetate, and copper(II) acetate, respectively, in place of cobalt(II) acetate.

Preparation of Acetophenone α-Methylbenzylhydrazone. A mixture of 1-bromo-1-phenylethane (50 g, 0.27 mol), 100 % hydrazine hydrate (103 g, 2.06 mol), triethylamine (50 ml), and benzene (100 ml) was refluxed for 6 h. The contents were then poured into an aqueous solution of sodium hydroxide and extracted five times with 400 ml of diethyl ether. After drying over Na_2CO_3 and removing the ether, the resulting α-methylbenzylhydrazine was purified by distillation (64.5—66.0 °C/1.6 mmHg); yield, 31.2 g (78 %); IR: 3280 cm^{-1} (N–H); and PMR: 1.24 ppm (methyl), 3.16 ppm (N–H), 3.66 ppm (methine), and 7.25 ppm (phenyl).

A mixture of α-methylbenzylhydrazine (31.2 g, 0.211 mol), acetophenone (25.3 g, 0.211 mol), acetic acid (40 mg), and anhydrous ethanol (50 ml) was purged with nitrogen and then refluxed for 12 h. After the solvent had been removed, a pale yellow viscous liquid was obtained; yield, 50 g (94 %); IR: 3275 cm^{-1} (N–H) and 1597 cm^{-1} (C=N); PMR: 2.02 ppm (a), 1.56 ppm (b), 4.55 ppm (c), 7.25 ppm (d), 7.55 ppm (e), and 4.87 ppm (f); and GC-MS: *m/e* (rel intensity), 238 (parent peak, 0.6), 237 (2.9), 222 (3.8), 133 (2.3), 118 (2.9), 105 (100), 104 (2.4), and 92 (2.3).



Decomposition of Azo Compound. A benzene solution of an Azo compound with or without a metal complex was charged into an ampoule and degassed twice by a freeze-thaw method to remove the oxygen; the ampoule was then sealed *in vacuo*. After standing at 104 °C in a light-shielded oil bath for 2 days, the contents of the ampoule were subjected to analysis.

Analysis of Decomposition Products. 2,3-Diphenylbutane was isolated from the decomposition products by using column chromatography (silica gel–hexane). It was identified by PMR: 1.01 ppm (methyl), 2.78 ppm (methine), and 7.20 ppm (phenyl); and GC-MS: *m/e* (rel intensity), 210 (parent peak, 1.1), 106 (9.5), 105 (100), 104 (25), 79 (4.4), and 77 (1.9).

It was not easy to isolate acetophenone α-methylbenzylhydrazone from the decomposition products because of the oxygen-sensitive nature of the hydrazone. Therefore, a reaction mixture was freeze-dried for six hours, and the remaining oily residue (C) was subjected to elemental analysis and PMR, GC-MS, and IR analyses. The oily residue (C) was found to be almost pure acetophenone α-methylbenzylhydrazone (purity 98 %, by GLC determination) when the thermolysis was carried out with the *RS*-Azo compound (512.1 mg) and Co(II)TPP (15.6 mg) in benzene (50 ml) at 104 °C. The PMR, GC-MS, and IR spectra of (C) agreed well with those of acetophenone α-methylbenzylhydrazone synthesized separately. Found: C, 80.76; H, 7.57; N, 11.09%. Calcd:** C, 80.57; H, 7.51; N, 11.65%.

Quantitative analyses of the products were carried out by means of GLC techniques using a column packed with Silicone DC-550. The column temperatures were 120 °C for ethylbenzene and styrene, 200 °C for 2,3-diphenylbutane, and 250 °C for acetophenone α-methylbenzylhydrazone. Benzene, the solvent, was used as the internal standard.

Measurement of Decomposition Rates. The decomposition rates of the azo compounds were measured in benzene using a differential pressure gauge at 70 °C. After the calculation of the rates, the vapor pressure of the benzene used as the solvent was corrected. AIBN: 3.7×10^{-5} mol l^{-1} s^{-1}, *SS*-Azo compound: 1.1×10^{-6} mol l^{-1} s^{-1}.

Measurement of ESR. The ESR of a benzene solution of the reaction mixture was measured under nitrogen at room temperature or at −196 °C. A benzene solution of Co(II)TPP and a mixture of Co(II)TPP and acetophenone α-methylbenzylhydrazone synthesized separately were measured in the manner described above.

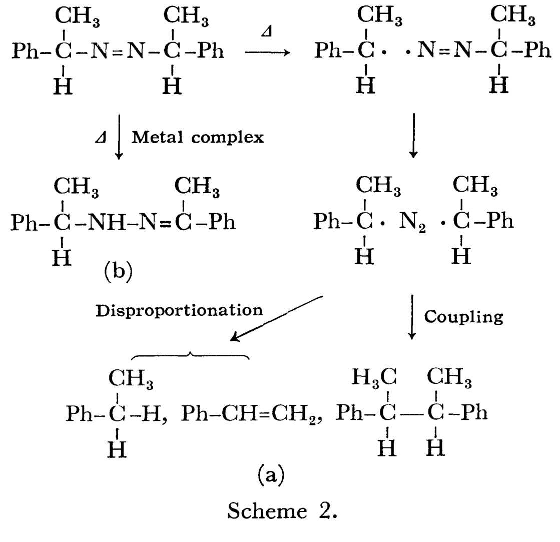
Measurement of the Specific Rotation of the Hydrogen-transfer Product. The *SS*-Azo compound (3.67×10^{-2} M) was decomposed in the presence of Co(II)TPP (6.3×10^{-5}—1.56×10^{-4} M) in benzene at 104 °C. An optical rotation of the benzene solution containing decomposition products was measured using a 100 mm quartz cell at 20 °C. The optical rotation was reduced to optically active products, especially the hydrogen-transfer product, based on a quantitative analysis of the products by means of GLC.

Results and Discussion

General Aspects of Decomposition. The yield distribution of the thermolysis products from 1,1′-diphenylazoethane (Azo compound) with or without a metal complex are summarized in Table 1. The products from the Azo compound by thermolysis in the presence of a metal complex are identified as ethylbenzene, styrene, 2,3-diphenylbutane, and acetophenone α-methylbenzylhydrazone (called hereafter the hydrogen-transfer product).

The hydrogen-transfer product is resistant to heat (unchanged at 104 °C for 10 days) or light (unchanged for 60 min under UV light), but it is very sensitive to oxygen and turns to acetophenone and 1-phenylethanol when placed in contact with oxygen.[8] Table 1 shows that the hydrogen-transfer product is formed in the presence of a metal complex such as Co(II)TPP or Co(II)$(sal)_2$(*R*-CHXDA) (Scheme 2(b)), and that the yield is increased with an increase in the concentration of the metal complex. The Azo compound was changed into the hydrogen-transfer product almost quantitatively with 1 mol % of Co(II)TPP for the Azo compound. No hydrogen-transfer product is produced in the absence of the metal complex.

The mode of the decomposition of the Azo compound without a metal complex, on the other hand, is shown in Scheme 2(a).[9] The decomposition products are styrene, ethylbenzene, and 2,3-diphenylbutane derived from the 1-phenylethyl radical.



Scheme 2.

** The values calculated in consideration of Co(II)TPP (15.6 mg) and the hydrogen-transfer product (512.1 mg) contained in (C).

TABLE 1. YIELDS OF PRODUCTS FROM 1,1'-DIPHENYLAZOETHANE BY THERMOLYSIS IN THE PRESENCE OF A METAL COMPLEX

Azo compd ($\times 10^2$ M)	Cobalt complex ($\times 10^4$ M)	$\frac{\text{Co complex.}}{\text{Azo compd}}$ (molar ratio) ($\times 10^3$)	Products (%) $Ph{-}CH_2CH_3$	$Ph{-}CH{=}CH_2$	$Ph{-}\underset{H}{\overset{CH_3}{C}}{-}\underset{H}{\overset{CH_3}{C}}{-}Ph$	$Ph{-}\overset{CH_3}{C}{=}N{-}NH{-}\overset{CH_3}{C}H{-}Ph$
SS 4.3	0	0	1.1	0.4	79.5	0
SS 4.3	CoTPP 0.38	0.88	0.7	0.6	36.5	59.8
SS 4.3	CoTPP 1.1	2.6	0.4	0.8	14.8	82.0
SS 4.3	CoTPP 3.4	7.9	0.3	1.7	5.9	91.1
SS 7.1	CoTPP 17	24	0.1	1.6	0	98.0
SS 4.7	Co* 11	23	2.0	1.3	50.8	29.5
SS 4.7	Co* 22	47	1.8	1.4	43.8	40.0
SS 6.7	Co* 40	60	2.0	1.8	55.9	41.1
SS 4.7	Co* 44	94	1.8	1.9	40.0	47.4
RR 4.6	Co* 11	24	2.0	1.3	52.2	25.1
RR 4.6	Co* 22	48	1.8	1.4	48.1	33.1
RR 4.6	Co* 44	96	1.8	1.9	46.8	35.1
RS 4.3	0	0	1.6	0.4	95.0	0
RS 3.7	CoTPP 3.0	8.1	0.4	1.6	6.4	89.5
RS 4.3	CoTPP 3.5	8.1	0.2	1.4	4.2	93.3
RS 5.3	CoTPP 6.4	12	0.1	1.8	0	98.0
RS 4.7	Co* 1.1	2.4	1.8	0.6	92.1	4.6
RS 4.8	Co* 2.3	4.7	2.0	0.7	91.2	8.4
RS 5.2	Co* 16	30	2.4	1.3	63.9	26.4
RS 5.6	Co* 23	41	2.4	1.4	68.4	18.5
RS 5.5	Co* 26	47	2.4	1.4	61.9	25.6
RS 4.5	Co* 52	114	2.1	2.4	43.2	45.8

Co*: Co(II)$(sal)_2$(*R*-CHXDA). Reaction Conditions: 104 °C, 2 days, in benzene (50 ml).

Stabilization of the Radical by Metal Complexes. The formation of the hydrogen-transfer product is not observed at room temperature, regardless of the presence of a metal complex in the reaction system. A comparison of the yield of the hydrogen-transfer product from the *SS*-Azo compound with Co(II)TPP in the presence and in the absence of AIBN at 70 °C is shown in Fig. 1. The rates of the decomposition reaction at 70 °C were found to be 3.7×10^{-5} M s^{-1} for AIBN and 1.1×10^{-6} M s^{-1} for the *SS*-Azo compound, AIBN being decomposed 34 times more rapidly than the *SS*-Azo compound. The radical concentration in the reaction system with AIBN should be much higher than that in the system without AIBN. As may be seen in Fig. 1, the rate of the formation of the hydrogen-transfer product is very high in the reaction system containing AIBN (A). This shows that a radical formation is necessary for the formation of the hydrogen-transfer product.

Table 2 shows the influence of the central metal and its ligand on the yield of the hydrogen-transfer product. The yields of the hydrogen-transfer product decreased in this order; Co>Ni>Mn>Cu, and TPP>$(sal)_2$(*R*-

TABLE 2. INFLUENCE OF THE CENTRAL METAL OF THE COMPLEXES ON THE YIELD OF THE HYDROGEN-TRANSFER PRODUCT

SS-Azo compd ($\times 10^2$ M)	Metal complex ($\times 10^3$ M)	Products (%) $Ph{-}CH_2CH_3$	$Ph{-}CH{=}CH_2$	$Ph{-}\underset{H}{\overset{CH_3}{C}}{-}\underset{H}{\overset{CH_3}{C}}{-}Ph$	$Ph{-}\overset{CH_3}{C}{=}N{-}NH{-}\overset{CH_3}{C}H{-}Ph$
8.45	CoTPP 8.04	0.2	1.4	8.9	88.0
8.45	NiTPP 8.04	0.5	0.3	34.7	53.6
8.45	MnTPP 8.10	0.9	0.4	60.8	41.3
8.45	CuTPP 8.00	1.2	1.2	91.5	3.2
4.3	Co* 13.2	2.0	1.3	48.8	34.6
4.3	Ni* 10.6	0.8	0.8	92.2	1.3
4.3	Mn* 15.5	0.8	1.0	90.6	1.0
4.3	Cu* 10.4	0.8	0.8	94.3	0.8

Co*, Ni*, Mn*, Cu*: Co(II), Ni(II), Mn(II), Cu(II)$(sal)_2$(*R*-CHXDA).
Reaction conditions: 104 °C, 2 days, in benzene (50 ml).

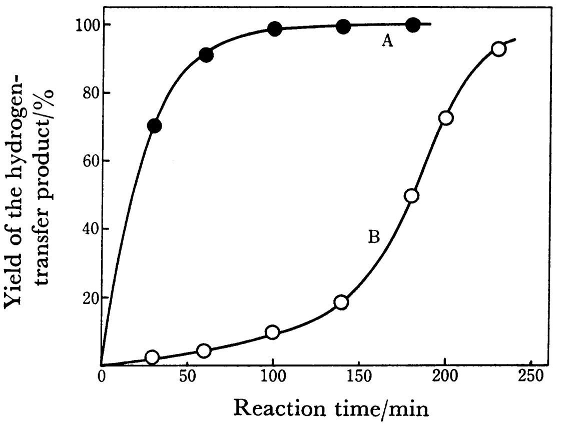
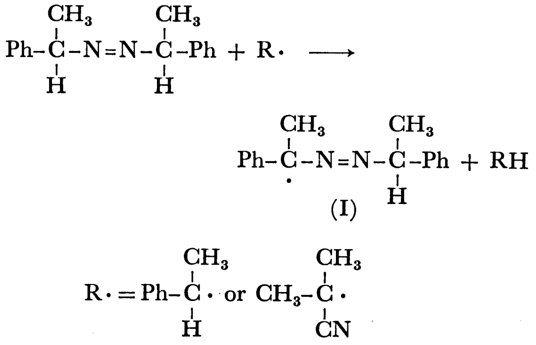


Fig. 1. Effect of AIBN on amount of acetophenone α-methylbenzylhydrazone formed.

	A	B
SS-Azo compd	8.9×10^{-2} M	8.4×10^{-2} M
Co(II)TPP	6.0×10^{-4} M	5.3×10^{-4} M
AIBN	2.1×10^{-2} M	0 M

Reaction Conditions: at 70 °C in benzene.

CHXDA). This order is in good agreement with that of the ability of metal complexes to stabilize 1-cyano-1,2-dimethylpropyl radical ($CH_3\underset{\cdot}{C}(CN)CH(CH_3)_2$), Co(II)-TPP>Ni(II)TPP>Mn(II)TPP>Cu(II)TPP.1) It may be supposed that the α-hydrogen of the Azo compound is easily abstracted by a radical. By the elimination of the α-hydrogen, Ph-$\underset{\cdot}{C}(CH_3)$-N=N-CH($CH_3$)-Ph (I) is produced as is shown below:

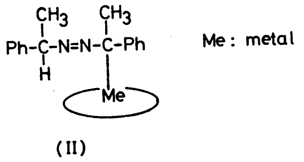


$$\mathrm{Ph{-}\underset{H}{\overset{CH_3}{C}}{-}N{=}N{-}\underset{H}{\overset{CH_3}{C}}{-}Ph} + R\cdot \longrightarrow \mathrm{Ph{-}\underset{\cdot}{\overset{CH_3}{C}}{-}N{=}N{-}\underset{H}{\overset{CH_3}{C}}{-}Ph} + RH$$

(I)

$$R\cdot = \mathrm{Ph{-}\underset{H}{\overset{CH_3}{C}}}\cdot \text{ or } \mathrm{CH_3{-}\underset{CN}{\overset{CH_3}{C}}}\cdot$$

It is considered that the dependence of the yield of the hydrogen-transfer product on kinds of metal complex is attributable to degree of interaction between radical(I) and the metal complex, that is, the stability of the intermediate(II) formed in the reaction system.



(II)

The ESR spectra of a reaction mixture which contains decomposition products from the *SS*-Azo compound in the presence of Co(II)TPP are shown in Fig. 2. A peak of Co^{II} was observed when the reaction mixture was measured at room temperature (a). At −196 °C, on the other hand, a characteristic octet of Co^{II} was observed, and each peak was split into a triplet, indicating the N-Co^{II} bond (b). Furthermore, a very small peak (g=2.001$_2$) was observed at −196 °C; the intensity of this peak increased upon irradiation with UV light (c). It is considered that the peaks in Figs. 2(a) and 2(b) are attributable to an intermediate(III) which has a cobalt nitrogen bond, while the peak in Fig. 2(c) is attributable to a radical(IV) formed possibly by the cleavage of the cobalt-nitrogen bond of the intermediate(III), as is shown below:

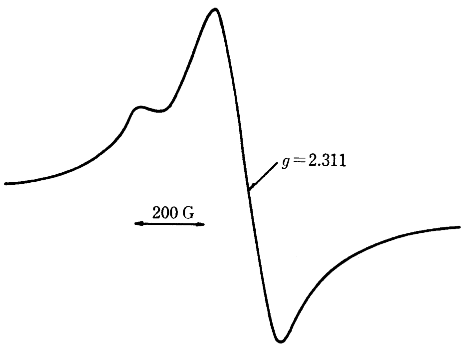


Fig. 2(a). ESR spectrum of reaction mixture of *SS*-Azo compound in the presence of Co(II)TPP at room temperature.

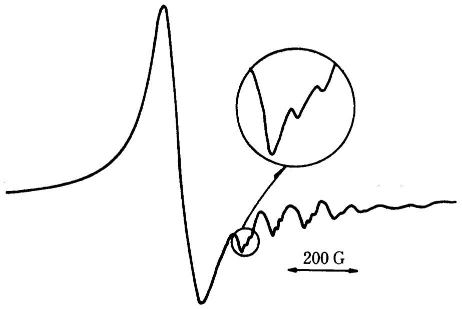


Fig. 2(b). ESR spectrum of reaction mixture of *SS*-Azo compound in the presence of Co(II)TPP at −196 °C.

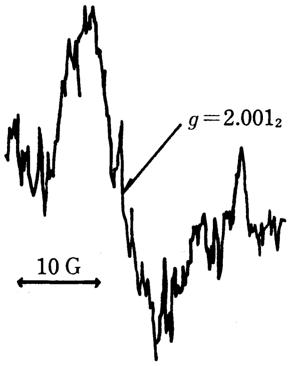
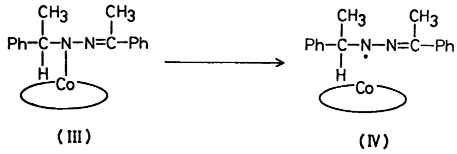


Fig. 2(c). ESR spectrum of reaction mixture of *SS*-Azo compound in the presence of Co(II)TPP at −196 °C.



(III) (IV)

In this connection, it should be noted that carbon-cobalt bond of alkyl cobalamine or vitamine B_{12} is cleaved by UV light.[10]

No peaks were observed, at room temperature, for either the benzene solution of Co(II)TPP only, or the benzene solution of Co(II)TPP and the hydrogen-transfer product synthesized separately. This means that the peaks in Fig. 2 can not result from an interaction of Co(II)TPP and the hydrogen-transfer product.

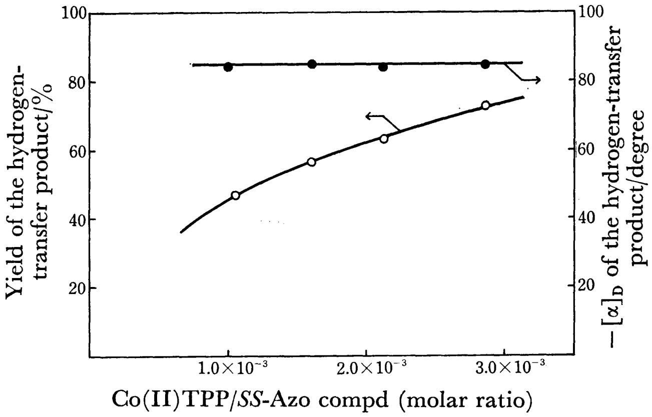
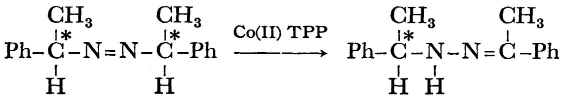


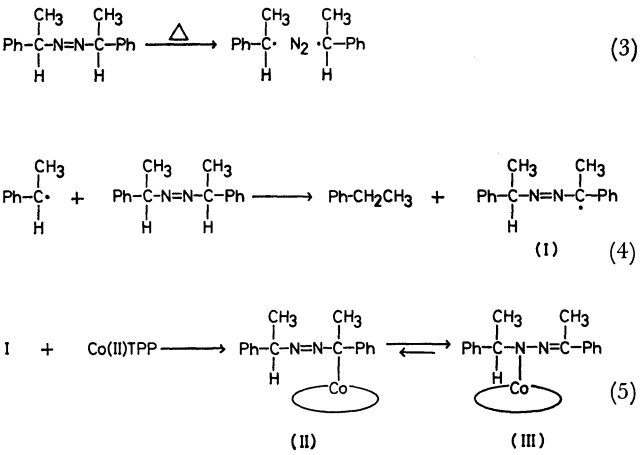
Fig. 3. Yield and specific rotation of the hydrogen-transfer product obtained from *SS*-Azo compound in the presence of Co(II)TPP in benzene at 104 °C for 2 days.

Stereochemistry of Acetophenone α-Methylbenzylhydrazone. The specific rotation of the hydrogen-transfer product, which was obtained from the *SS*-Azo compound by thermolysis in the presence of Co(II)TPP, was almost constant ($[\alpha]_D = -88°$), regardless of its yield (Fig. 3). This means that the configuration of one of the two asymmetric carbons of the original *SS*-Azo compound is probably retained in the hydrogen-transfer product.



$$\mathrm{Ph{-}\overset{CH_3}{\underset{H}{C^*}}{-}N{=}N{-}\overset{CH_3}{\underset{H}{C^*}}{-}Ph \xrightarrow{Co(II)\,TPP} Ph{-}\overset{CH_3}{\underset{H}{C^*}}{-}\underset{H}{N}{-}N{=}\overset{CH_3}{C}{-}Ph}$$

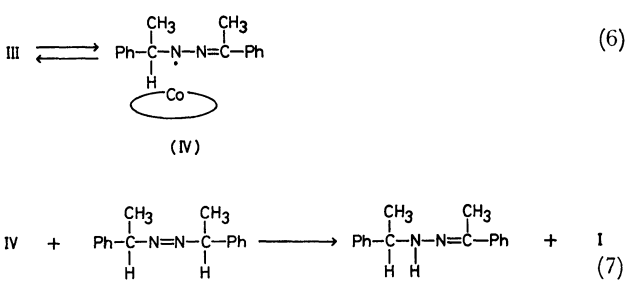
A Possible Mechanism:



$$\mathrm{Ph{-}\overset{CH_3}{\underset{H}{C}}{-}N{=}N{-}\overset{CH_3}{\underset{H}{C}}{-}Ph \xrightarrow{\Delta} Ph{-}\overset{CH_3}{\underset{H}{C}}\cdot\ \ N_2\ \ \cdot\overset{CH_3}{\underset{H}{C}}{-}Ph} \tag{3}$$

$$\mathrm{Ph{-}\overset{CH_3}{\underset{H}{C}}\cdot + Ph{-}\overset{CH_3}{\underset{H}{C}}{-}N{=}N{-}\overset{CH_3}{\underset{H}{C}}{-}Ph \longrightarrow Ph{-}CH_2CH_3 + \underset{(I)}{Ph{-}\overset{CH_3}{\underset{H}{C}}{-}N{=}N{-}\overset{CH_3}{\underset{\cdot}{C}}{-}Ph}} \tag{4}$$

$$\mathrm{I + Co(II)TPP \longrightarrow \underset{(II)}{Ph{-}\overset{CH_3}{\underset{H}{C}}{-}N{=}N{-}\overset{CH_3}{\underset{Co}{C}}{-}Ph} \rightleftarrows \underset{(III)}{Ph{-}\overset{CH_3}{\underset{H}{C}}{-}\underset{Co}{N}{-}N{=}\overset{CH_3}{C}{-}Ph}} \tag{5}$$



$$\mathrm{III \rightleftarrows \underset{(IV)}{Ph{-}\overset{CH_3}{\underset{\underset{Co}{H}}{C}}{-}\underset{\cdot}{N}{-}N{=}\overset{CH_3}{C}{-}Ph}} \tag{6}$$

$$\mathrm{IV + Ph{-}\overset{CH_3}{\underset{H}{C}}{-}N{=}N{-}\overset{CH_3}{\underset{H}{C}}{-}Ph \longrightarrow Ph{-}\overset{CH_3}{\underset{H}{C}}{-}\underset{H}{N}{-}N{=}\overset{CH_3}{C}{-}Ph + I} \tag{7}$$

Scheme 3 is a step in which radicals are released by thermolysis. In the beginning, the concentration of the radical is very low; therefore, scarcely no coupling and disproportionation reactions of the diffusion radicals occurs, and the diffusion radical formed abstracts the α-hydrogen of the Azo compound (Scheme 4). The radical(I) thus formed is immediately stabilized by a cobalt complex (Scheme 5) or abstracts the α-hydrogen from another Azo compound to form the radical(I) again. However, the latter mechanism is not probable in the light of the results shown in Fig. 3. The intermediate(II) undergoes a rearrangement reaction to the intermediate(III), in which a nitrogen-cobalt bond is newly formed. The intermediates(II) and (III) are presumably equilibrated with each other (Scheme 5). The existence of the intermediate(III) is suggested by the results of the ESR spectra, shown in Fig. 2. The series of steps from Scheme 4 to Scheme 7 is a chain reaction.

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