

COBALT(II) TETRAPHENYLPORPHYRIN-CATALYZED ISOMERIZATION OF
ELECTRONEGATIVE SUBSTITUTED QUADRICYCLANES

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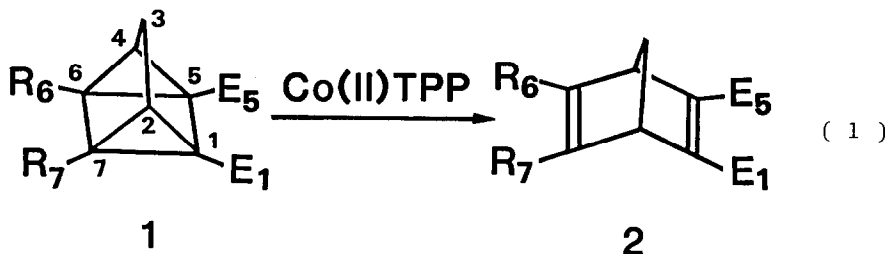
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Summary: Co(II)TPP¹-catalyzed isomerization of a series of electronegative substituted quadricyclanes(1) to the corresponding norbornadiene(2) was found to proceed via radicophilic attack of the metal to 1.

Metal-catalyzed isomerization of highly strained system, particularly quadricyclane to norbornadiene, has been of considerable interest from theoretical and experimental viewpoints.² However, the known examples are mostly limited within the reactions initiated by an electrophilic attack of metals to bent σ -bonds, and it has been regarded as likely that Lewis-basicity of the bent σ -bond is one of the most important factor determining reactivity.³ Recently, our interest has been directed toward seeking a suitable catalyst for the cycloreversion of electronegative substituted quadricyclanes as solar energy storage system.⁴ In this connection, we wish to describe our finding that Co(II)TPP catalyzes the isomerization of electronegative substituted quadricyclane (1) via radicophilic attack of the metal.

Quadricyclanes were selected so that the kinetic comparison of the catalyzed isomerization within the series would provide fundamental informations about the electronic requirement for the interaction of Co(II)TPP with the quadricyclanes. The series of the derivatives (1b-1h) were prepared by photo-irradiation of the corresponding norbornadienes (2), which were obtained by usual manner (Diels-Alder reaction) employing appropriate cyclopentadienes and acetylenic compounds.⁵ Co(II)TPP was prepared according to the method of Adler.⁶

The isomerization of 1 catalyzed by the Co(II)TPP was carried out in benzene under argon. Special cautions for anaerobic condition⁷ were taken in handling the reaction systems so as to eliminate a possibility for Co(II)TPP to be oxidized by molecular oxygen, because there has been some disagreement⁸ about the valency state of the metal of real active species.



- a: $E_1 = E_5 = R_6 = R_7 = H$
 b: $E_1 = CO_2Me$, $E_5 = R_6 = R_7 = H$
 c: $E_1 = CN$, $E_5 = R_6 = R_7 = H$
 d: $E_1 = E_5 = CO_2Me$, $R_6 = R_7 = H$
 e: $E_1 = E_5 = CN$, $R_6 = R_7 = H$
 f: $E_1 = CO_2Me$, $E_5 = R_7 = H$, $R_6 = Me$
 g: $E_1 = CO_2Me$, $E_5 = R_6 = H$, $R_7 = Me$
 h: $E_1 = E_5 = CO_2Me$, $R_6 = R_7 = Me$

In all the cases shown in eq. 1, a quantitative cycloreversion of 1 to 2 was observed. The catalyzed isomerization of 1 was followed kinetically⁷ in d_6 -benzene by integration of the appropriate olefinic ¹H-NMR signal(s) for 2 formed. Pseudo-first-order kinetic plots $\ln([1]_{init.}/[1])$ vs reaction time) were found to be linear for each case of the reactions. The reactions were proved to be first-order also with respect to the catalyst. Pseudo-first-order and second-order rate constants (k_1^{obsd} and k_2 , respectively) for the isomerization at 27°C are shown in Table 1.

In contrast to usual cases of metal catalyzed isomerizations of strained molecules, which may well be related to the π -like character of bent σ -bond with low ionization potential,^{3b} in the present isomerization of 1 catalyzed by Co(II)TPP, introduction of an electron-withdrawing substituent E_1 (CO_2Me , CN) at C_1 causes an enhancement of the rate constants as shown in Table 1 (entry 1,2 and 3). Additional substitution at C_5 by E_5 , however, causes a lowering of the rate constants (entry 2 \rightarrow 5 and 3 \rightarrow 8).

The unusual variation in the reactivity with changing substitutional modification can be explained only based on a corner-metalated radical intermediate (Figure 1) caused via radicophilic attack of Co(II)TPP to the carbon of the most radicofugal property. The electron-withdrawing group at C_1 and the electron-donating cyclopropyl moiety ($C_5C_6C_4$) should serve to stabilize the radical⁹ induced on C_1 via a radicophilic attack of Co(II)TPP at C_7 . Additional substitution of C_5 by E_5 would reduce the dative nature of

Table 1 Pseudo-First-Order Rate Constants (k_1^{obsd}) and Second-Order Rate Constants (k_2) of the TPPCo(II)-promoted Isomerization of $\underline{1}^{\text{a}}$.

Entry	Quadri- cyclane($\underline{1}$)	[$\underline{1}$] (M)	10^5 [TPPCo(II)] (M)	$10^4 k_1^{\text{obsd}}$ (sec^{-1})	k_2 ($\text{M}^{-1}\text{sec}^{-1}$)
1	<u>1a</u>	0.1	5.0	3.1	6.2
2	<u>1b</u>	0.1	5.0	6.6	13
3	<u>1c</u>	0.1	5.0	5.0	10
4	<u>1d</u>	0.1	1.0	0.50	5.0
5	<u>1d</u>	0.1	5.0	3.0	6.0
6	<u>1d</u>	0.1	50	30	6.0
7	<u>1d</u>	0.05	5.0	3.1	6.2
8	<u>1e</u>	0.1	5.0	1.3	2.6
9	<u>1f</u>	0.1	5.0	0.85	1.7
10	<u>1g</u>	0.1	5.0	0.0085	0.017
11	<u>1h</u>	0.1	5.0	0.0027	0.0054

a) The reaction was kinetically followed in d_6 -benzene under argon at 27 ± 1 °C. Experimental error is within + 5%.

the $C_5C_6C_4$ to give a negative influence on the rate of the isomerization.

Radical character of d^7 -metals has been pointed out by Hoffmann in his concept of "Isolobal Analogy".¹⁰ In this case of Co(II)TPP, the radicophilic character may well be due to the odd electron in the d_z^2 orbital.¹¹ In connection with the attacking site of Co(II)TPP, it is noteworthy that the substitution by methyl group provides a much greater rate retarding effect at C_7 than at C_6 position (see entry 9 and 10).

Further work on the catalysis behavior of Co(II) porphyrins is under way.

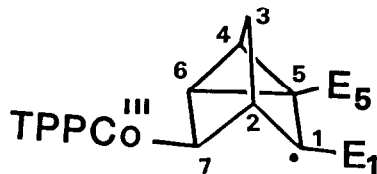


Figure 1

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