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Co(II)PORPHYRIN CATALYZED ISOMERIZATION OF BICYCLOBUTANECARBONITRILE

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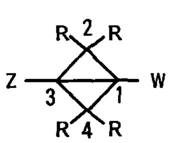
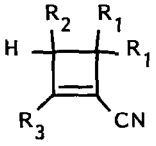
Summary: In the presence of catalytic amount of TPPCo(II), bicyclobutane-1-carbonitrile easily isomerized to cyclobutene-1-carbonitrile in 60-70 % yield. Reaction behavior of other electronegative substituted bicyclobutanes in the presence of TPPCo(II) was also investigated.

Transition-metal complex catalyzed isomerization of bicyclobutanes has been a subject of much controversy, and the mechanistic feature of the reactions has been investigated extensively using metals such as Ag(I), Zn(II), Hg(II), Rh(I), Ir(I), Pd(II), Cu(I), Ru(II), and Pt(IV).[1] Although the reaction mode is dependent on the metals and the ligands of the catalyst complex, examples studied so far are mostly confined to the cases in which the isomerization proceeds via the initial cleavage of an edge bond of the carbocycles. Thus, to date other type of the reaction mode, for example, catalyzed isomerization by central bond fission remains to be explored.

Here, we wish to describe our finding on a new type of the reaction of bicyclobutane derivatives (**1**) in the presence of catalytic amount of TPPCo(II) [2] via the initial fission of the central bond.



1



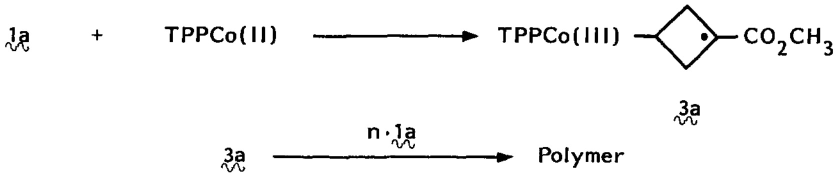
2

1a: W=CO_2CH_3, R=Z=H
1b: W=CN, R=Z=H
1c: W=CO_2CH_3, R=H, Z=CH_3
1d: W=CN, R=H, Z=CH_3
1b-d_4: W=CN, R=D, Z=H

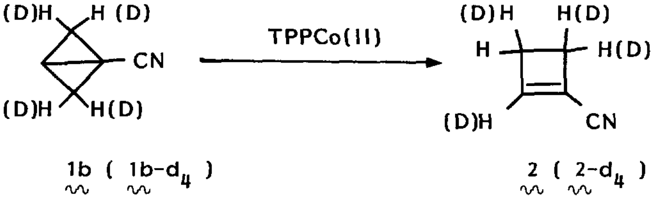
2: $R_1=R_2=R_3=H$
2-d_1: $R_2=D$, $R_1=R_3=H$
2-d_3: $R_1=R_3=D$, $R_2=H$
2-d_4: $R_1=R_2=R_3=D$

Various bicyclobutane derivatives (**1a** - **1d**) were synthesized by the modifications of literature procedures.[3] The TPPCo(II) catalyzed reaction of **1** was carried out in benzene under reflux with a positive argon pressure after deaerating pretreatment of the system by freeze and thaw cycles. The reaction of **1a** in both the presence and the absence of TPPCo(II) afforded polymer products. The disappearance rate of **1a** was followed by a gas chromatography with biphenyl as an internal standard. The rate of the disappearance of **1a** was much larger in the presence of 0.1 equiv. of TPPCo(II) than in the catalyst absence.[4] As shown in Scheme I, the polymerization could be initiated by TPPCo(II) via C_1-C_3 bond fission by attacking of the catalyst to C_3 of **1a**. Free radical initiated polymerization of **1a** was studied in detail by Wiberg [5] and the above result may be due to the radicalphilic property of TPPCo(II).[6,7]

Scheme I



On the other hand, the reaction feature of **1b** was quite different from that of **1a**. The reaction of **1b** in the presence of 0.1 equiv. of TPPCo(II) in benzene under reflux for 95 hr [4] gave cyclobutene-1-carbonitrile (**2**) in 60 - 70 % yield together with minor polymer product. In order to get insight into the reaction, the TPPCo(II) catalyzed reaction of 2,2,4,4-tetradeuterocyclobutane-1-carbonitrile (**1b**-d_4)[8] was carried out. The reaction of **1b**-d_4 afforded 2,3,4,4-tetradeuterocyclobutene-1-carbonitrile (**2**-d_4). This result excludes the possibility of formation of **2** via "path γ " described by Paquette.,[9] and the formation of **2** is considered to involve both C_1-C_3 and C-H bond cleavage and hydrogen shift.

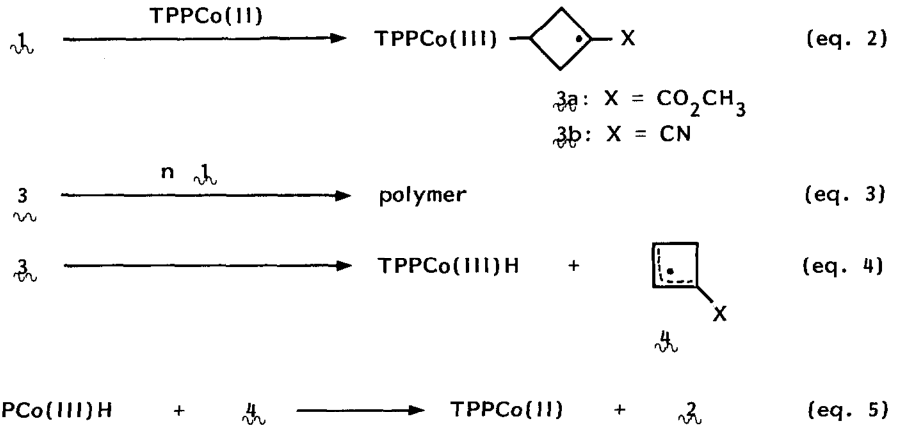


(eq.1)

When a mixture of 1b and **1b**-d_4 (1/1) was heated in the presence of TPPCo(II) the product distribution with respect to deuterium scrambling was **2** : **2**-d_1 : **2**-d_3 : **2**-d_4 = 3 : 1.5 : 2 : 1,[10] indicating that the hydrogen shift do occur intermolecularly.

Whole the experimental results could be reasonably explained in terms of the radical mechanism shown in Scheme II, in which the incipient radical **3** produced by the radical-philic attack of TPPCo(II) to C_3 of **1** is proposed as a key intermediate for both the formation of **2** and polymerization of **1**. As is the case of **1a** (X = CO_2CH_3) in eq 3, **3** play a role as an initiator of the radical polymerization. On the other hand, the much stabilized radical **3b** with CN would preferably undergo β-Co-H *elimination*[11] (eq. 4) to give TPPCo(III)H and **4**, and subsequently **4** would abstract hydrogen from TPPCo(III)H to give final product.[12] The fact that the major product was monomeric indicates that the radical **3b** and **4** (X=CN) should be less reactive toward **1b**.

Scheme II



In connection with the attacking site of the catalyst, it should be notable that *bridge-head methylated derivatives,* **1c** *and* **1d**, *did not react in the reaction condition employed.* The similar phenomenon has been observed in the case of TPPCo(II) catalyzed isomerization of quadricyclanes to norbornadienes.[6] The rate retardation of ca. 10^{-3} has been observed *when quadricyclanes were substituted with methyl group at the carbon of the attacking* site. Although we don't have full explanation about the difference in reaction feature between **1a** and **1b**, it seems likely that the difference in radical stabilizing ability between CO_2CH_3 *in* **1a** *and CN in* **1b** *could be a factor.*

In the context of biological interest of square-plannar cobalt complex,[13] it should be of significance to be pointed out that the present reaction is prototype for a *square-plannar Co(II) complex to catalyze an organic reaction involving C-C and C-H bond* cleavages and intermolecular hydrogen transfer.

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(4) In a typical run, solution of **1** of the concentration of 70 mM was used.

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(8) 2,2,4,4-Tetradeuterobicyclobutane-1-carbonitrile, **1b**-d_4 , was prepared according to Scheme III, in which H/D exchange reaction of 3-oxo-cyclobutane-1-carbonitrile in D_2O was carried out two times repeatedly. **1b**-d_4: ^{1}H-NMR 2.40 ppm (broad s). IR (neat) 3090, 2200 cm^{-1}. MS m/e 55(100), 83 M^+(98). The perdeutero derivative has been prepared by Hall and his co-workers[3] by tediously long synthetic rout.

(9) Paquette,L.A.; Zon,G.,J.Am.Chem.Soc., **1974**,96,203.

(10) The product distribution was determined on the basis of the mass spectrum of the GC fraction for cyclobutene-1-carbonitriles.

(11) In case of closely related alkylcobalamines, those possessing hydrogen in the β-position are known to undergo spontaneous decomposition by way of β-elimination. Schrauzer, G.N.; Grate,J.H., J.Am.Chem.Soc.,**1981**,103,541. J.Am.Chem.Soc.,**1979**,101,4601.

(12) Similar participation of TPPCo(III)H has been assumed in a certain hydrogen transfer reaction by Tsuruta et. al..[7]

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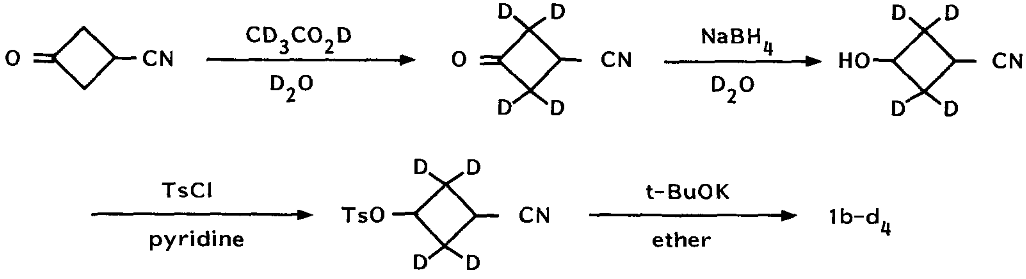
Scheme III[8]



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