Catalytic Reactions of *cis*-But-2-en-1,4-diol with Iridium Complexes: Formation of *trans*-Crotonaldehyde

Chong Shik Chin*, Byeongno Lee, and Jun Ho Shin

Department of Chemistry, Sogang University, Seoul 121-742. Received April 8, 1989

In the presence of appropriate catalytic systems, unsaturated alcohols undergo various reactions, such as dehydrogenation,[1] dehydration,[2] cyclization,[3] isomerization,[4] hydrogenolysis,[5] disproportionation,[6] and decarbonylation.[7] Most catalytic systems are effective for a certain reaction of a substrate,[1-5] while some metal complexes catalyze several reactions simultaneously.[6,7] During the investigation for the catalytic activities of iridium and rhodium complexes, we found that some iridium(I)[9a] and rhodium(I)[8,9b] complexes catalyze some reactions of unsaturated alcohols such as isomerization (double bond migration),[8] dehydrogenation, and hydrogenolysis.[9b,10] In this paper, we wish to report unusual consecutive catalytic reactions (dehydrogenation, hydrogenolysis and *cis-trans* isomerization) of *cis*-but-2-en-1,4-diol (**1**) to give *trans*-crotonaldehyde (**2**) in the presence of either $Ir(ClO_4)(CO)(PPh_3)_2$ (**3**) or $Ir(H)_2(ClO_4)(CO)(PPh_3)_2$ (**4**) under nitrogen (equation 1).

$$\underset{\mathbf{1}}{cis\text{-}HOCH_2CH{=}CHCH_2OH} \longrightarrow \underset{\mathbf{2}}{trans\text{-}CH_3CH{=}CHCHO} + H_2O \qquad (1)$$

Figures 1a and 1b show the catalytic formation of **2** reactions of **1** with **3** and **4**, respectively. It is noticed in both Figures 1a and 1b that *cis*-$CH_3CH=CHCHO$ (**5**) is produced and then isomerized to the final product, **2**. Since it has been already known 'that at room temperature under nitrogen, complex **3** catalyzes dehydrogenation of unsaturated alcohols to give unsaturated aldehydes and **4** which then catalyzes the hydrogenolysis of unsaturated alcohols to produce unsaturated hydrocarbons,[9a,10] it is conceivable that the intermediate **5** seen in Figure 1a is the hydrogenolysis product of *cis*-$HOCH_2CH=CHCHO$ (**6**) formed in the dehydrogenation of **1** by **3**. Accordingly, the following reaction steps are readily suggested for the formation of **2**. One may consider complex 4 (but not **3**) being the actual catalyst for the isomerization of 5 to 2 since 4 is known to be the actual catalyst for the isomerization of unsaturated alcohols to saturated aldehydes even when 3 is initially used as the catalyst.[9a] In separate experiments, however, we found that 4 does not catalyze the isomerization of 5 to 2.

$$\underset{\mathbf{1}}{cis\text{-}HOCH_2CH{=}CHCH_2OH} \xrightarrow[-\ Ir(H)_2(ClO_4)(CO)(PPh_3)_2\ (4)]{Ir(ClO_4)(CO)(PPh_3)_2\ (3)} \underset{\mathbf{6}}{cis\text{-}HOCH_2CH{=}CHCHO} \xrightarrow[-\ 3,\ -H_2O]{4} \underset{\mathbf{5}}{cis\text{-}CH_3CH{=}CHCHO} \xrightarrow{3} \underset{\mathbf{2}}{trans\text{-}CH_3CH{=}CHCHO} \qquad (2)$$

Reactions of 1 with 4 are also explained by the reaction steps listed in equation 2 although they are not in the same order as in equation 2. Hydrogenolysis of **1** would apparently occur first to produce **3** and *cis*-$CH_3CH=CHCH_2OH$ (**7**) when complex 4 is used as the catalyst. Then dehydrogenation of **7** is followed to give **4** and **5** (seen in Figure 1b) which is finally isomerized to **2** by **3** (equation 3).

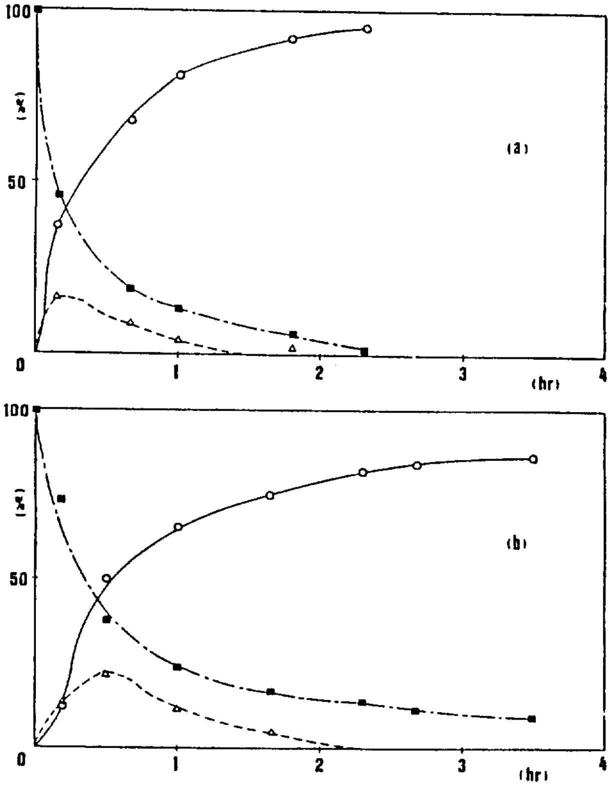


Figure 1. Catalytic reaction of *cis*-But-2-en-1,4-diol (**1**) (0.2 mmol) with (a) $Ir(ClO_4)(CO)(PPh_3)_2$ (**3**) (0.02 mmol) and (b) $Ir(H)_2(ClO_4)(CO)(PPh_3)_2$ (**4**) (0.02 mmol) in $CDCl_3$ (0.4 m*l*) and CD_3OD (0.1 m*l*) Under Nitrogen at 45 °C. —■-■—, *cis*-$HOCH_2CH=CHCH_2OH$ (**1**); —△-△—, *cis*-$CH_3CH=CHCHO$ (**5**); —○-○—, *trans*-$CH_3CH=CHCHO$ (**2**).

$$\mathbf{1} \xrightarrow[-3,\ -H_2O]{4} \underset{\mathbf{7}}{cis\text{-}CH_3CH{=}CHCH_2OH} \xrightarrow[-4]{3} \mathbf{5} \xrightarrow{3} \mathbf{2} \qquad (3)$$

Formation of *trans*-crotonaldehyde (**2**) seems somewhat slower with **4** than with, **3**, which may be understood in terms of relative amounts of **3** available for the last step (**5**→**2**) present in the reaction mixture. Complex 3 is required consequtively for both of the dehydrogenation (**7**→**5**) and isomerization (5→**2**) in equation 3 while complex 3 is consumed in every other reaction of dehydrogenation (**1**→**6**) and isomerization (**5**→**2**) in equation 2.

Experiment. Product (*cis*-$CH_3CH=CHCHO$) and *trans*-$CH_3CH=CHCHO$) analysis were carried out by comparing ^1H NMR signals with those of authentic samples.

Acknowledgment. Authors wish to thank the Korean Science and Engineering Foundation and the Ministry of Education, Republic of Korea for the financial support to this study.

References

1. (a) Y. Matsumura, K. Hashimoto, and S. Yoshida, *J. Chem. Soc. Chem. Commun.*, 1599 (1987); (b) D. Morton and D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.*, 248 (1987); (c) J. G. Wadkar and R. V. Chaudhari, *J. Mol. Catal.*, **22**, 103 (1983).
2. T. Nishiguchi, N. Machida, and E. Yamamoto, *Tetrahedron Lett.*, **28**, 4565 (1987).
3. J. V. Commasseto, H. M. C. Ferraz, N. Petragnani, and C. A. Brandt, *Tetrahedron Lett.*, **28**, 5611 (1987).
4. (a) T. Tatsumi, K. Hashimoto, H. Tominaga, Y. Mizuta, K. Hata, M. Hidai, and Y. Uchida, *J. Organomet. Chem.*, **252**, 105 (1983). (b) J. V. N. Vara Prasad and C. N. Pillai, *J. Catal.*, **88**, 418 (1984). (c) A. V. Musheegyan, V. Kh. Ksipteridis, A. O. Gukasyan, O. A. Kamalyan, G. G. Grigoryan, *Kinet. Katal.*, **25**, 81 (1984). (d) Y. Sasson and G. L. Rempel, *Tetrahedron Lett.*, 4133 (1974).
5. R. Durand, P. Genete, C. Moreau, and J. L. Pirat, *J. Catal.*, **90**, 147 (1984).
6. J. Blum, *J. Mol. Catal.*, **3**, 33 (1977).
7. A. Emery, A. C. Oehschlager, and A. M. Unrau, *Tetrahedron Lett.*, **50**, 4401 (1970).
8. (a) C. S. Chin, S. Y. Lee, J. Park, and S. Kim, *J. Am. Chem. Soc.*, **110**, 8244 (1988). (b) C. S. Chin, J. Park, C. Kim, S. Y. Lee, J. H. Shin, and J. B. Kim, *Catal. Lett.*, **1**, 203 (1988).
9. (a) C. S. Chin, J. H. Shin, and J. B. Kim, *J. Organomet. Chem.*, **356**, 381 (1988). (b) J. Park and C. S. Chin, *Bull. Korean Chem. Soc.*, **8**, 324 (1987).
10. Unpublished results.

Thermal Conversion of S,S-Bis(2-Pyrimidinyl and 2-Pyridinyl) Dithiocarbonates to Bis(2-Pyrimidinyl and 2-Pyridinyl) Sulfides

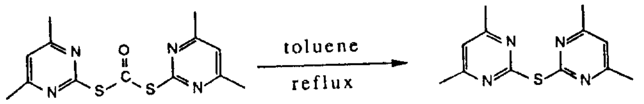
Sunggak Kim* and Sung Soo Kim

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-012.

Received April 13, 1989

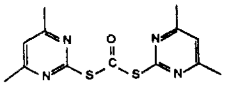
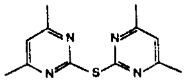
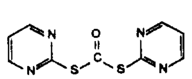
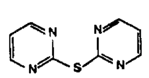
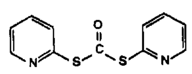
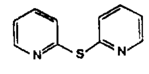
While examining the method for the esterification of carboxylic acids under essentially neutral conditions using condensing agents,[1] it has been found that S,S-bis(4,6-dimethyl-2-pyrimidinyl) dithiocarbonate (DPDC)[2] is cleanly converted into bis(4,6-dimethyl-2-pyrimidinyl) sulfide in refluxing toluene.

Reaction of phenylacetic acid with equimolar amounts of benzyl alcohol and DPDC in refluxing acetonitrile for 5 h gave benzyl phenylacetate in 41% yield together with a significant amount of the byproduct. Based on elemental analysis, as well as mass, IR and ^{1}HNMR spectra, it was reasonable to assign the byproduct into bis(4,6-dimethyl-2-pyrimidinyl) sulfide. Furthermore, its melting point was in accord with that of the reported compound.[3]



Among the solvents tested in this study, toluene was found to be the most effective. The reaction was complete within 4 h in refluxing toluene, whereas the reaction required 24 h for completion in refluxing acetonitrile. Tetrahydrofuran and dichloromethane were totally ineffective and the addition of 4-dimethylaminopyridine did not effect the present reaction. Thus, S,S-bis(2-pyrimidinyl and 2-pyridinyl) dithiocarbonates were cleanly converted into bis(2-pyrimidinyl and 2-pyridinyl) sulfides in 96% and 70% yield, respectively in refluxing toluene. The experimental results are shown in Table 1. However, this type of reaction could not be applied to di-2-pyridyl carbonate[4] and bis(4,6-dimethyl-2-mercaptopyrimidinyl) oxalate.[5] Di-2-pyridyl carbonate was completely decomposed to 2-hydroxypyridine in refluxing toluene for 20 h, whereas bis(4,6-dimethyl-2-mercapto pyrimidinyl) oxalate was thermally inert. Although several methods for the synthesis of bis(2-pyrimidinyl and

Table 1. Preparation of Bis(2-pyrimidinyl and 2-pyridinyl) Sulfides[a]

Substrate	Time, h	Product	Isolated yield, %
	4		93
	8		96
	30		70

[a] Reacted in refluxing toluene.