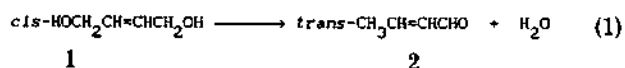


Catalytic Reactions of *cis*-But-2-en-1,4-diol with Iridium Complexes: Formation of *trans*-Crotonaldehyde

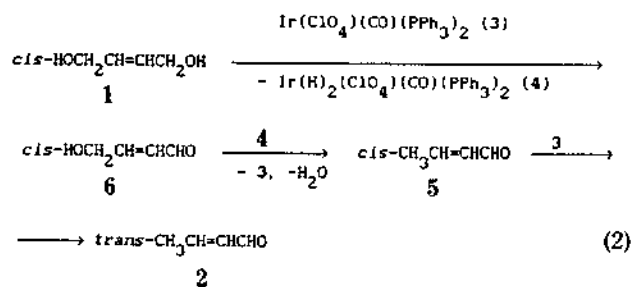
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In the presence of appropriate catalytic systems, unsaturated alcohols undergo various reactions, such as hydrogenation,¹ dehydration,² cyclization,³ isomerization,⁴ hydrogenolysis,⁵ disproportionation,⁶ and decarbonylation.⁷ Most catalytic systems 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.^{9a,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(ClO₄)(CO)(PPh₃)₂ (**3**) or Ir(H)₂(ClO₄)(CO)(PPh₃)₂ (**4**) under nitrogen (equation 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*-CH₃CH=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*-HOCH₂CH=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**.

Reactions of **1** with **4** are also explained by the reaction steps listed in equation 2 although they are not in the same

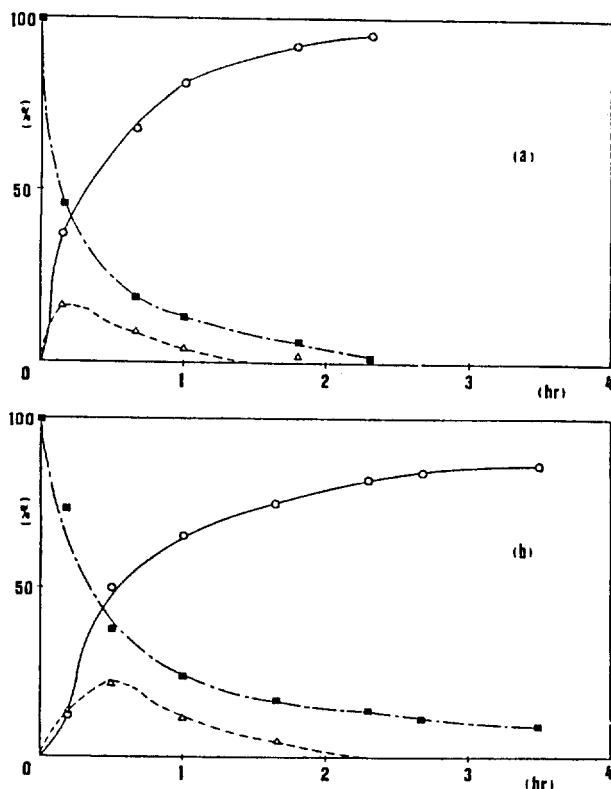
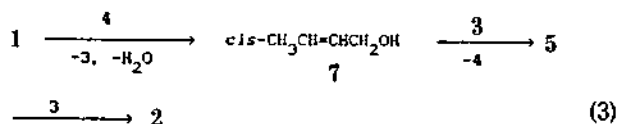


Figure 1. Catalytic reaction of *cis*-But-2-en-1,4-diol (**1**) (0.2 mmol) with (a) Ir(ClO₄)(CO)(PPh₃)₂ (**3**) (0.02 mmol) and (b) Ir(H)₂(ClO₄)(CO)(PPh₃)₂ (**4**) (0.02 mmol) in CDCl₃ (0.4 ml) and CD₃OD (0.1 ml) Under Nitrogen at 45 °C. —■—, *cis*-HOCH₂CH=CHCH₂OH (**1**); —△—, *cis*-CH₃CH=CHCHO (**5**); —○—, *trans*-CH₃CH=CHCHO (**2**).

order as in equation 2. Hydrogenolysis of **1** would apparently occur first to produce **3** and *cis*-CH₃CH=CHCH₂OH (**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).



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 consecutively 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*-CH₃CH=CHCHO) and *trans*-CH₃CH=CHCHO) analysis were carried out by comparing ¹H NMR signals with those of authentic samples.

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

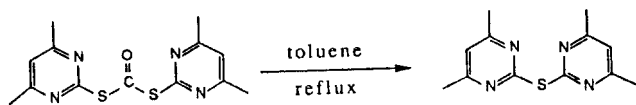
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While examining the method for the esterification of carboxylic acids under essentially neutral conditions using condensing agents,¹ it has been found that S,S-bis(4,6-dimethyl-2-pyrimidinyl) dithiocarbonate (DPDC)² is cleanly converted into bis(4,6-dimethyl-2-pyrimidinyl) 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 ¹H NMR 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-pyrimi-

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

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

^aReacted in refluxing toluene.

dinyl 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 carbonate⁴ 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-mercaptopyrimidinyl) oxalate was thermally inert. Although several methods for the synthesis of bis(2-pyrimidinyl and