

**Preliminary communication**

**REARRANGEMENT OF 2-BUTYNE-1,4-DIOL TO BUTYROLACTONE  
CATALYZED BY RUTHENIUM COMPLEXES**

YOUVAL SHVO\*, YIGAL BLUM and DEBORAH RESHEF

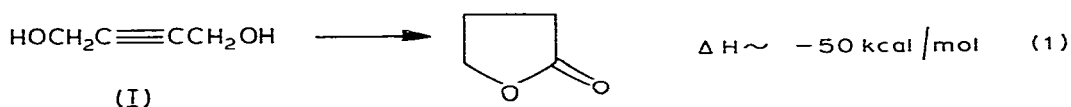
*Department of Chemistry, Tel-Aviv University, 69978 Tel Aviv (Israel)*

(Received July 2nd, 1982)

**Summary**

The isomerization of 2-butyne-1,4-diol to butyrolactone catalysed by ruthenium complexes is described.

The differential enthalpy of 2-butyne-1,4-diol (I) and butyrolactone (II), which are isomers, is ca. 50 kcal/mol. Yet the former do not spontaneously revert to the latter and are we not aware of any example of a chemically induced rearrangement. The high exothermicity of the reaction stems from the large heat of formation of the triple bond, but a substantial kinetic energy barrier must separate the two isomers. Mechanistically, such a rearrangement must certainly be a complex multi-step process. It can be regarded as disproportionation reaction which formally calls for the transfer of 4H atoms from the hydroxymethyl groups to the triple bond.



We reasoned that such a transformation might possibly be induced by transition metal catalysts. Our recent findings [1,2], as well as those of Murahashi [3], prompted us to examine the activity of several H-transfer catalysts toward 2-butyne-1,4-diol. The results are presented in Table 1.

Dodecacarbonyltriruthenium gave a poor yield of butyrolactone [4], in spite of the fact that reaction of the diol was practically quantitative. Although competitive polyester formation may have taken place [2], the isolation of an impure solid with *m/e* 258, assigned to hexa(hydroxymethyl)benzene, indicates a competitive trimerization of I. Deeming et al. [5] recently

TABLE 1<sup>a</sup>

## RESULTS FOR THE CONVERSION 2-BUTYNE-1,4-DIOL → BUTYROLACTONE

Catalyst (mmol)	I (mmol)		Solvent (g) <sup>b</sup>	Temperature (°C)	Time (h)	Yield (%) <sup>c</sup>
1 RuH <sub>2</sub> (PPh <sub>3</sub> ) <sub>4</sub>	0.27	7.0	Diglyme(6.6)	145	3 12	21 49
2 RuH <sub>2</sub> (PPh <sub>3</sub> ) <sub>4</sub>	0.27	7.0	Diglyme(6.0)	110	12	21
3 RuH <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	0.27	7.0	1-Methylnaphthalene (6.0)	180	6	36
4 RuH <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	0.3	7.0	Diglyme(6.2)	145	1.5 6.5	17 30
5 Ru <sub>3</sub> (CO) <sub>12</sub>	0.05	8.5	Diglyme(2.0)	145	4	5
6 RuCl <sub>3</sub>	0.10	7.5	Diglyme(6.0)	145	20	3
7 RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	0.05	7.0	Diglyme(6.0)	150	10	1

<sup>a</sup> The reaction was carried out in a glass-lined autoclave under argon. <sup>b</sup> All solvents were dried and distilled. <sup>c</sup> The yields of butyrolactone were determined by GLC using an internal standard calibration curve.

isolated and characterized several complexes from stoichiometric reaction of Ru<sub>3</sub>(CO)<sub>12</sub> and I, but did not report the formation of butyrolactone. RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and RuCl<sub>3</sub>, either alone or with added triphenylphosphine, are inefficient in the conversion I→II (Table 1). However, RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> [6] and RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> [6] give reasonable yields of butyrolactone, up to 49%, under various reaction conditions (Table 1).

Both intra- and intermolecular hydrogen transfer are compatible with the above transformation. Butyrolactone was obtained in 40% yield in the reaction of Ru<sub>3</sub>(CO)<sub>12</sub> with *cis*-1,4-butenediol. Obviously, the double bond in the above compound cannot accommodate the transfer of 4H atoms. The very formation of butyrolactone from butenediol indicates that at least some of the H-transfer must occur via an intermolecular pathway. Thus, it is logical to invoke similar behavior for reaction 1.

If reaction 1 is confined to an intramolecular H-transfer pathway, the following sequence of transformations induced by the active catalytic species can be envisaged:



This hypothesis is supported by three important experimental observations: (a) Aldehydes are intermediates in the catalytic oxidative coupling reaction of alcohols [1,2] with Ru<sub>3</sub>(CO)<sub>12</sub>. (b) 2-Hydroxytetrahydropyrans and 2-hydroxytetrahydrofurans are oxidized to the corresponding lactones under catalytic H-transfer conditions [7]. (c) The *cis* mode of addition of hydrogen to a triple bond was observed in H-transfer reactions with Ru<sub>3</sub>(CO)<sub>12</sub> [8].

Similar intermediates may be invoked for the intermolecular reaction mode. Alternatively, succindialdehyde, formed by the disproportionation of I, may cyclize to butyrolactone in a Tishchenko type reaction [9]; both steps must be induced by a catalyst. However, we have excluded a Tishchenko type reac-

tion in the oxidative coupling of simple alcohols with  $\text{Ru}_3(\text{CO})_{12}$  [2]. The mechanism of this and related reactions is being currently investigated.

Finally, we note that the modest yields of butyrolactone does not detract from the remarkable nature of the isomerization. Further optimization of the reaction conditions, as well as a search for other catalysts, may improve the efficiency of this reaction.

**Acknowledgement.** We thank the Johnson Matthey Chemicals Ltd. for a generous loan of ruthenium trichloride.

## References

- 1 Y. Blum, D. Reshef and Y. Shvo, *Tetrahedron Lett.*, **22** (1981) 1541.
- 2 Y. Shvo, Y. Blum, D. Reshef and M. Menzin, *J. Organometal. Chem.*, **226** (1981) C21.
- 3 S-I. Murahashi, K-I. Ito, T. Naota and Y. Maeda, *Tetrahedron Lett.*, **22** (1981) 5327.
- 4 Butyrolactone was identified by GLC, NMR and IR.
- 5 S. Aime, A. Tiripicchio, M.T. Camellini and A.J. Deeming, *Inorg. Chem.*, **20** (1981) 2027.
- 6 J.J. Levinson and S.D. Robinson, *J. Chem. Soc. A*, (1970) 2947.
- 7 L. Cottier, G. Descotes and J. Sabadie, *J. Mol. Cat.*, **7** (1980) 337; G. Descotes and J. Sabadie, *ibid.*, **5** (1979) 415; M. Bianchi, G. Menchi, F.F. Francalanci and F. Piacenti, *J. Organometal. Chem.*, **188** (1980) 109.
- 8 Y. Shvo, unpublished results.
- 9 H. Horino, T. Ito and A. Yamamoto, *Chem. Letters*, (1978) 17.