A Simple Route to α,β-Unsaturated Aldehydes from Prop-2-ynols

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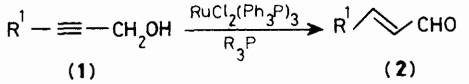
2-Ynols can be isomerized stereoselectively to (2*E*)-enals with a ruthenium complex as catalyst.

The conversion of 2-ynols to 2-enals is one of the processes in the synthesis of natural products owing to the easy accessibility of ynols.[1] The usual approach consists of reduction with lithium aluminium hydride (LAH) followed by oxidation with a suitable metal oxide; this requires multiple steps and often leads to considerable amounts of environmentally hazardous wastes.[2] This conversion can be regarded as isomerization at the triple bond. Corey reported the isomerization of oct-2-yn-1-ol to oct-2-enal using n-butyl-lithium.[3] However, this procedure required the conversion of the 2-ynols to ether derivatives and also produced a mixture of oct-2-enal and the prop-2-ynic starting materials. On the other hand, transition metal catalysts offer a mild approach for hydrogen migrations and so much attention has been directed towards the use of these catalysts in the isomerization of alkenic alcohols.[4] Much work relating to the intermolecular hydrogen transfer reactions between acetylenes and alcohols has been reported.[5] Surprisingly 2-ynols have not been employed as starting materials for this synthetically useful isomerization reaction. Recently, we studied the isomerization of 2-ynones to conjugated dienones[6] and of 2-ynoic esters to dienoic esters;[7] we found that ruthenium complexes and aliphatic phosphine ligands were effective in these reactions. Here we wish to report the $RuCl_2(Ph_3P)_3 + R_3P$ catalysed isomerization of 2-ynols to (2*E*)-enals (equation 1).

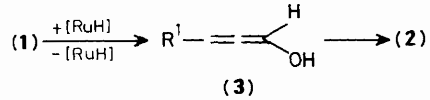
The following procedure was typical. A solution of 2-ynol [(**1**), 5 mmol], $RuCl_2(Ph_3P)_3$ (0.1—0.2 mmol), and R_3P (0—0.4 mmol) in toluene (5 ml) was heated at reflux for about 36 h. After removal of the solvent, (2*E*)-enal (**2**) was isolated by distillation at reduced pressure and then passed through a column of silica gel. G.c. and ^1H n.m.r. spectroscopy showed that the product consisted of more than 95% of the *E*-isomer. The results are shown in Table 1. In the absence of a ligand, or using Ph_3P as the ligand, the reaction did not occur (entries 1 and 2), also Pr^i_3P is found to be a more effective ligand than Bu^n_3P (compare entries 3 and 4 of Table 1). It is also found that 2-ynols with an aryl group are less reactive than those with an alkyl group (compare entries 3 and 8).

The mechanism of this reaction may be similar to that of the isomerization of 2-ynones to dienones.[6] Ruthenium hydride species may be formed first from the reaction of prop-2-ynols and $RuCl_2(Ph_3P)_3$.[8] After the addition and elimination of Ru–H, 1,2-dienol (**3**) was formed, which may further tautomerize to (**2**) (equation 2). Although two other examples of reactions of but-2-yne-1,4-diol which yield heterocycles have

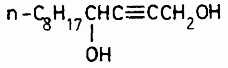


(**1**) (**2**) 1

a; $R^1 = n\text{-}C_6H_{13}$
b; $R^1 = n\text{-}C_5H_{11}$
c; $R^1 = n\text{-}C_7H_{15}$
d; $R^1 = n\text{-}C_4H_9$
e; $R^1 = C_6H_5$

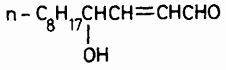


(**3**) 2



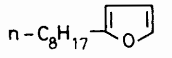
$n\text{-}C_8H_{17}CH(OH)C{\equiv}CCH_2OH$

(**4**)

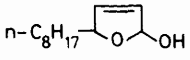


$n\text{-}C_8H_{17}CH(OH)CH{=}CHCHO$

(**5**)



(**6**)



(**7**)

Table 1. Isomerization of 2-ynols to 2-enals catalysed by $RuCl_2(Ph_3P)_3 + R_3P$.

Entry	2-ynol	Mol% cat.	R_3P	R_3P/cat.	*t*/h	Yield/%[a]
1	(**1a**)	2	—	0	30	0[b]
2	(**1a**)	2	Ph_3P	2	30	0[b]
3	(**1a**)	2	Bu^n_3P	2	36	72[b]
4	(**1a**)	2	Pr^i_3P	2	32	80
5	(**1b**)	2	Pr^i_3P	2	36	82
6	(**1c**)	2	Pr^i_3P	2	36	85
7	(**1d**)	2	Pr^i_3P	2	36	78
8	(**1e**)	4	Bu^n_3P	2	48	63

[a] Isolated yield. [b] Determined by ^1H n.m.r. spectroscopy.

been reported,[9] this reaction is, to our knowledge, the first example of isomerization of 2-ynols to the simple enals catalysed by a transition metal complex.

Under the same conditions, dodec-2-yne-1,4-diol (**4**) could isomerize regio- and stereo-selectively to give 4-hydroxy-(2*E*)-dodecen-1-al (**5**) in 44% yield; in addition, a small amount of 2-octylfuran (**6**) was isolated in 14% yield. A possible route of formation of 2-octylfuran may be first through an intramolecular cyclization of (**5**) to give the hemiacetal (**7**), followed by dehydration to yield (**6**).[8,9]

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References

1 A. B. Shenvi and H. Gerlach, *Helv. Chim. Acta*, 1980, **63**, 2426; E. J. Corey, H. Park, A. Barton, and Y. Nii, *Tetrahedron Lett.*, 1980, **21**, 4243; H. Tanaka, K. Yoshida, Y. Itoh, and H. Imanaka, *ibid.*, 1981, **22**, 3421; T. Nakamura, M. Namiki, and K. Ono, *Chem. Pharm. Bull.*, 1987, **35**, 2635.

2 J. Muzart, *Tetrahedron Lett.*, 1987, **28**, 4665 and references cited therein.

3 E. J. Corey and S. Terashima, *Tetrahedron Lett.*, 1972, 1815.

4 P. A. Chaloner, 'Handbook of Co-ordination Catalysis in Organic Chemistry,' Butterworth, London, 1986, p. 417.

5 R. A. W. Johnstone, A. H. Wilby, and I. D. Entwistle, *Chem. Rev.*, 1985, **85**, 129.

6 D. Ma, Y. Lin, X. Lu, and Y. Yu, *Tetrahedron Lett.*, 1988, **29**, 1045; D. Ma, Y. Yu, and X. Lu, *J. Org. Chem.*, 1989, **54**, 1105.

7 D. Ma and X. Lu, *Tetrahedron Lett.*, 1989, **30**, 843.

8 Y. Blum, D. Reshef, and Y. Shvo, *Tetrahedron Lett.*, 1981, **22**, 1541; S.-I. Murahashi, T. Naota, K. Ito, Y. Maeda, and H. Taki, *J. Org. Chem.*, 1987, **52**, 4319.

9 Y. Shvo, Y. Blum, and D. Reshef, *J. Organomet. Chem.*, 1982, **238**, C79; Y. Tsuji, Y. Yokoyama, K. Huh, and Y. Watanabe, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3456.