Isomerisation of Allyl Ethers Catalysed by the Cationic Iridium Complex [Ir(cyclo-octa-1,5-diene)($PMePh_2$)$_2$]PF_6. A Highly Stereoselective Route to *trans*-Propenyl Ethers

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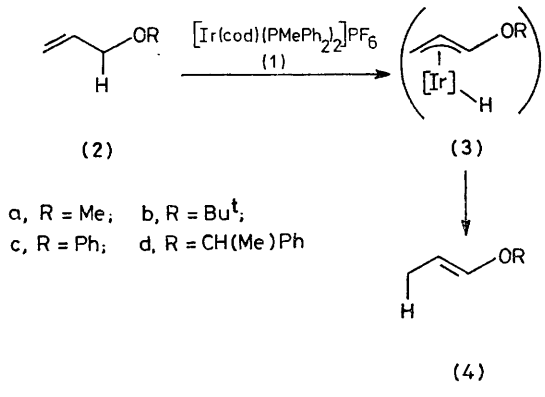
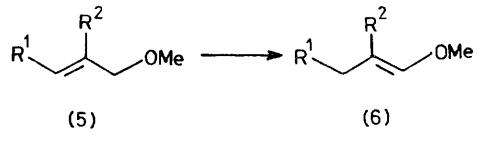
Summary Allyl alkyl (and aryl) ethers are isomerised by H_2-activated [Ir(cyclo-octa-1,5-diene)($PMePh_2$)$_2$]PF_6 in tetrahydrofuran or dioxan at room temperature to the corresponding *trans*-propenyl ethers (yields $\geqslant$ 95%; stereoselectivity $\geqslant$ 97%).

THE red air-stable cationic iridium complex[1] [Ir(cod)($PMePh_2$)$_2$]PF_6 (**1**; cod = cyclo-octa-1,5-diene), 'activated' by dihydrogen, is a very active catalyst for the isomerisation of allylic alcohols to aldehydes and ketones.[2] Here we report that the isomerisation of allyl ethers (**2**) with this catalytic system leads stereoselectively, and under mild conditions, to the corresponding *trans*-propenyl ethers (**4**); the substituted allylic ethers (**5a**) and (**5b**) are also isomerised.





a; R^1 = H, R^2 = Me
b; R^1 = Me, R^2 = H

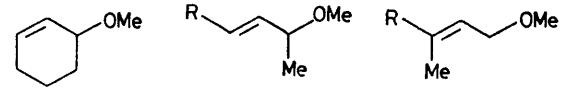
When a mixture of the catalyst (**1**) (6 μmol) and allyl ether (**2**) or (**5**) (*ca.* 5 mmol) in peroxide-free tetrahydrofuran or 1,4-dioxan (5 ml) is degassed and placed under H_2 at room temperature, the catalyst is 'activated' (presumably by hydrogenation of the cod ligand)[3] and the red suspension is replaced by a colourless solution; to effect the isomerisation, this solution is again degassed and left at room temperature under N_2. Both solvents gave almost identical results; those obtained in tetrahydrofuran are shown in the Table.

TABLE. Isomerisation of allyl ethers to enol ethers catalysed by [Ir(cod)($PMePh_2$)$_2$]PF_6 at room temperature in tetrahydrofuran.[a]

Allyl ether	Time/h[b]	Enol ether[c]	% Yield[d]	% Stereoselectivity
(**2a**)	0·5	(**4a**)	97	98
(**2b**)	0·5	(**4b**)	98	$\geqslant$98[e]
(**2c**)	4	(**4c**)	95	97
(**2d**)	3	(**4d**)	95[f]	97
(**5a**)	0·5	(**6a**)	98	—
(**5b**)[g]	2	(**6b**)	96	98

[a] Conditions: see text. [b] There was no further change after this time. [c] Isolated by distillation or preparative g.l.c., and identified by n.m.r. spectroscopy [L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon Press, New York, 1969, p. 302: J(CH=CH *trans*) *ca.* 12 Hz; J(CH=CH *cis*) *ca.* 6 Hz. The *cis*-enol ethers were obtained from the *trans*-isomers by equilibration (T. Okuyama, T. Fueno, and J. Furukawa, *Tetrahedron*, 1969, **25**, 5409)]. [d] Determined by g.l.c.; the only other detectable products were the *cis*-enol ether and the starting allyl ether. [e] The *cis*-isomer and (**2b**) were not resolved by g.l.c. under our conditions. [f] With 0·5 ml of cyclohexene in the reaction mixture; without cyclohexene, the yield was 71% at room temperature and 95% at 65 °C. [g] Containing *ca.* 5% of the *cis*-isomer; at the end of the reaction, the remaining 2% of allyl ether was a 1 : 1 mixture of (**5b**) and its *cis*-isomer.

The most striking features of this reaction are (a) its very high stereoselectivity (*trans*/*cis* > 30), (b) the very mild conditions and low concentration of catalyst required, and (c) the fact that it appears to be essentially limited to primary allyl ethers of the types (**2**) and (**5**) shown. Even at 65 °C, the secondary ethers (**7**) and (**8**, R = H and Me) were entirely unaffected, and the primary ethers (**9**) having a *cis* methyl group on the double bond were isomerised either to a very small extent (**9**, R = H), or not at all (**9**, R = Me). This great difference in reactivity could be useful for the selective removal of allylic groups in carbohydrate chemistry.[4]



(**7**) (**8**) (**9**)

The reaction almost certainly involves a π-allyl hydrido intermediate[5] (**3**) since [1,1-$^2H_2$]allyl methyl ether (*cf.* **2a**) gave the *trans* propenyl methyl ether (*cf.* **4a**) deuteriated on C-3 (and C-1), but *not* on C-2. It seems that, probably for steric reasons, the central metal atom can only accommodate a π-allyl unit with a *syn*-configuration, as in (**3**), *i.e.*, a configuration such that only hydrogen atoms occupy the '*endo*' positions. An intermediate (**3**) with this configuration (a) can only lead to a *trans*-enol ether (**4**) or (**6**), and (b) can only be formed from primary allylic ethers of types (**2**) and (**5**); primary ethers (**9**) with a *cis*-substituent on the double bond, and secondary ethers (**7**) and (**8**), would give π-allyl intermediates with at least one '*endo*' substituent, and hence do not react.

Many catalytic systems have been described for the isomerisation of allylic ethers.[6,7] They often require fairly vigorous conditions, and they all lead either stereoselectively to the *cis*-enol ether,[6,8] or to a mixture of *cis*- and *trans*-isomers.[7] The isomerisation reported here appears to be the first stereoselective conversion of allyl into *trans*-propenyl ethers.[8,9]

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[8] With one exception: the base-catalysed isomerisation of *cis*-cinnamyl methyl ether gives *trans*-1-methoxy-3-phenylpropene (I. Elphimoff-Felkin and J. Huet, *Compt. rend.*, 1969, **268C**, 2210).
[9] For an alternative route to *trans*-propenyl ethers, see: P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. N. Misra, and G. P. Withers, *J. Amer. Chem. Soc.*, 1977, **99**, 1993.