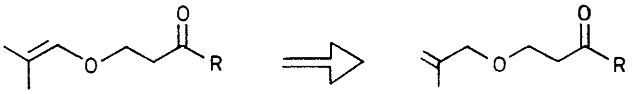
Isomerisation of Allyl Ethers to Vinyl Ethers catalysed by Palladium on Carbon

By HOWARD A J CARLESS* and DAVID J HAYWOOD
(*Department of Chemistry, Birkbeck College, Malet Street, London* WC1E 7HX)

Summary Several allyl ethers are cleanly converted into the corresponding prop-1-enyl ethers on heating in benzene or toluene in the presence of palladium on carbon.

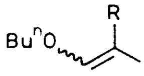
THE preparation of vinyl ethers has become important,[1] both in terms of the synthetic use of the aliphatic Claisen rearrangement,[2] and in the use of metallated derivatives of vinyl ethers as 'masked' acyl equivalents[3] In the carbohydrate field, especially, allyl ethers have been used as selective protecting groups for alcohols,[4] the first step in their removal often requires isomerisation to the vinyl ether, followed by hydrolysis[5] We now report that several allyl and methallyl (2-methylallyl) ethers are converted into the corresponding prop-1-enyl ethers in high yield under neutral conditions in the presence of catalytic amounts of palladium-on-carbon, by heating in benzene or toluene as solvent

During investigations of the photochemical reactions of unsaturated aldehydes,[6] we required a synthesis of the vinyl ether aldehyde (**1**) An attractive route to (**1**) appeared to be isomerisation of the methallyloxy-aldehyde (**2**) However, common existing methods for isomerisation of allyl to vinyl ethers were incompatible with the presence of the aldehyde functional group, such methods include

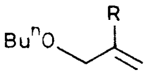


(1) R = H
(3) R = Me

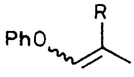
(2) R = H
(4) R = Me



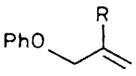
(5) R = H
(7) R = Me



(6) R = H
(8) R = Me

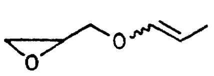


(9) R = H
(11) R = Me

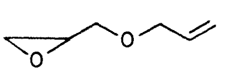


(10) R = H
(12) R = Me

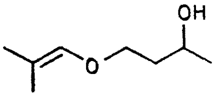
treatment of the allyloxy compound with strong base (KOBu^t, Me$_2$SO, heat),[7] or the use of tris(triphenylphosphine)rhodium(I) chloride[8,9] which can cause decarbonylation of aldehydes[10] Encouraged by a report[11] that acidic, methanolic solutions containing Pd/C can be used



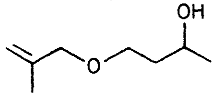
(13)



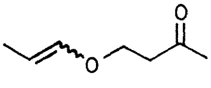
(14)



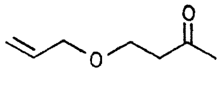
(15)



(16)



(17)



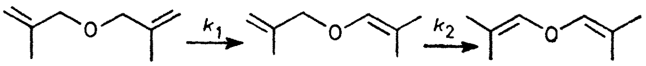
(18)

to remove the allyl ether protecting group, we have found that palladium on carbon alone converts (**2**) into (**1**) in high yield, on refluxing in benzene as solvent. The generality of this isomerisation method is shown by the examples in the Table. It is applicable not only to alkyl and aryl allyl ethers [(**6**), (**8**), (**10**), and (**12**)] but is also compatible with molecules containing one of a variety of functional groups, such as the epoxide (**14**), the alcohol (**16**), or the ketones (**4**) and (**18**). After reaction, separation of the catalyst requires the minimal step of filtration, and aqueous work-up is thus avoided. The present method is superior to the use of inorganic complexes such as $PdCl_2(PhCN)_2$, which failed to isomerise (**12**) to (**11**) even in refluxing xylene.[12,13] The Table shows that both allyl and methallyl ethers are isomerised to prop-1-enyl and 2-methylprop-1-enyl ethers, respectively; this is in contrast to the action of tris(triphenylphosphine)ruthenium(II) dichloride, which did not isomerise methallyl ethers.[14] Allyl ethers are converted mainly into *cis*-prop-1-enyl ethers (Table), and in this respect the use of palladium-on-carbon resembles several other isomerisation methods.[4,12,15]

TABLE. Isomerisation of allyl ethers catalysed by palladium on carbon.[a]

Starting material	Product[b]	Yield[c] (%)	Reaction time/h	Solvent	*cis*:*trans* product ratio
(**2**)	(**1**)	95	8	Benzene	—
(**4**)	(**3**)	97,82[d]	18	Toluene	—
(**6**)	(**5**)	75[d]	5	Benzene	64:36
(**8**)	(**7**)	95	5	Benzene	—
(**10**)	(**9**)	97	60	Toluene	69:31
(**12**)	(**11**)	80[d]	140	Toluene	—
(**14**)	(**13**)	93	12	Benzene	77:23
(**16**)	(**15**)	65	17	Benzene	—
(**18**)	(**17**)	93	4	Toluene	76:24

[a] Reaction conditions: starting material (2 g), 10% palladium on activated carbon (0·5 g) (Aldrich) in solvent (10 ml), heated under reflux with stirring under nitrogen. [b] All products were separated and identified by ^1H (and, in some cases, ^{13}C) n.m.r. spectra. [c] Yields estimated by g.l.c., unless otherwise stated. [d] Isolated yield



(19) (20) (21)

SCHEME

Noting that the isomerisation of *phenyl* allyl ethers (**10**) and (**12**) was apparently slow, we have investigated differences in the rates of the two isomerisation steps arising from the bis(methallyl) ether (**19**). Under our conditions, $k_1/k_2 = 6$ (Scheme), and this has allowed the very easy preparation of the previously unknown allyl vinyl ether (**20**)[16] (>75% of the crude material, after heating under reflux for 3·5 h in benzene). Further heating under reflux (21 h) gave the bis(2-methylprop-1-enyl) ether (**21**) in 86% yield from (**19**). The temperature required for isomerisation is sufficiently low that (**20**) does not undergo a competing Claisen rearrangement.

We thank the S.R.C. for financial support.

(*Received 7th July*, 1980; *Com.* 734.)

---

[1] For recent examples, see C. Earnshaw, C. J. Wallis, and S. Warren, *J. Chem. Soc., Perkin Trans.* 1, 1979, 3099; F. Barbot and P. Miginiac, *Helv. Chim. Acta*, 1979, **62**, 1451.

[2] S. J. Rhoads and N. R. Raulins, *Org. React.*, 1975, **22**, 1; F. E. Ziegler, *Acc. Chem. Res.*, 1977, **10**, 227; G. B. Bennett, *Synthesis*, 1977, 589.

[3] J. E. Baldwin, G. A. Höfle, and O. W. Lever, *J. Am. Chem. Soc.*, 1974, **96**, 7125.

[4] See R. Gigg, *J. Chem. Soc., Perkin Trans.* 1, 1980, 738, and references therein.

[5] J. Gigg and R. Gigg, *J. Chem. Soc.* (*C*), 1966, 82.

[6] H. A. J. Carless and D. J. Haywood, *J. Chem. Soc., Chem. Commun.*, 1980, 657, and unpublished results.

[7] P. A. Gent, R. Gigg, and R. Conant, *J. Chem. Soc., Perkin Trans.* 1, 1972, 248.

[8] E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1973, **38**, 3224.

[9] P. A. Gent and R. Gigg, *J. Chem. Soc., Chem. Commun.*, 1974, 277.

[10] H. M. Walborsky and L. E. Allen, *J. Am. Chem. Soc.*, 1971, **93**, 5465; however, *cf.* ref. 9.

[11] R. Boss and R. Scheffold, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 558.

[12] P. Golborn and F. Scheinmann, *J. Chem. Soc., Perkin Trans.* 1, 1973, 2870.

[13] Isomerisation of allyl ethers to prop-1-enyl ethers has been reported using the less readily available cationic iridium complex, $[Ir(cyclo\text{-}octa\text{-}1,5\text{-}diene)(PMePh_2)_2]PF_6$ (D. Baudry, M. Ephritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, 1978, 694) and using platinum(II)-hydrido complexes (H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1973, **12**, 1566).

[14] J. M. Reuter and R. G. Salomon, *J. Org. Chem.*, 1977, **42**, 3360.

[15] T. J. Prosser, *J. Am. Chem. Soc.*, 1961, **83**, 1701; C. C. Price and W. H. Snyder, *ibid.*, p. 1773.

[16] Compound (**20**) has previously been proposed as an intermediate in the acid-catalysed elimination of isobutyraldehyde dimethallyl acetal to yield 2,2,4-trimethylpent-4-enal: K. C. Brannock, *J. Am. Chem. Soc.*, 1959, **81**, 3379.