Wittig Rearrangements of Allyl Vinylcyclopropylmethyl Ethers

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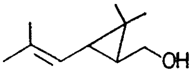
Summary Anions derived from allyl vinylcyclopropylmethyl ethers (**2**) rearrange by competing [1,2], [1,4], homo [2,5], and homo [4,5] sigmatropic changes to give allylic alcohols (**4**) and (**9**) and aldehydes (**5**) and (**6**); the hydrocarbon (**8**) results from a radical dissociation–recombination process.

BASE induced Wittig rearrangements of benzyl allyl and bisallyl ethers are well documented, and have been the subject of considerable mechanistic study.[1] By contrast, few studies have been made of related rearrangements of benzyl and allyl ethers of cyclopropylmethanols.[2] We describe results of a study of the Wittig rearrangements of allyl ethers derived from the vinylcylopropylmethyl alcohol (**1**) (chrysanthemyl alcohol).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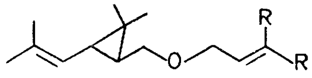
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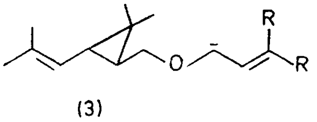
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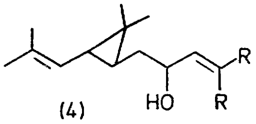
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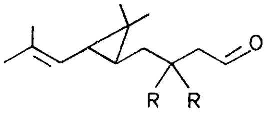
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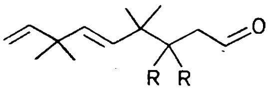
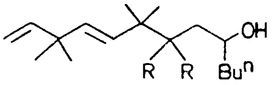

(6)

(a), R = H ; (b), R = Me

Treatment of the *trans*-ether (**2a**) with Bu^{n}Li in tetrahydrofuran at −20 °C led to a mixture of products which were isolated by liquid chromatography and identified as the hydrocarbon (**8**) (17%), the allylic alcohols (**4a**) (32%) and (**9a**) (11%), the secondary alcohol (**10a**) (18%), and *trans*-chrysanthemyl alcohol (**1**) (32%). Reaction between the corresponding *cis*-cyclopropylmethyl ether and Bu^{n}Li led to an identical mixture of products [with preservation of the *cis*-geometry about the cyclopropane rings in (**1**), (**4**), and (**10**)] in comparable proportions.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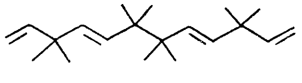
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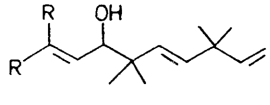
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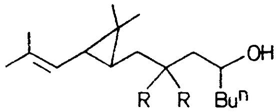
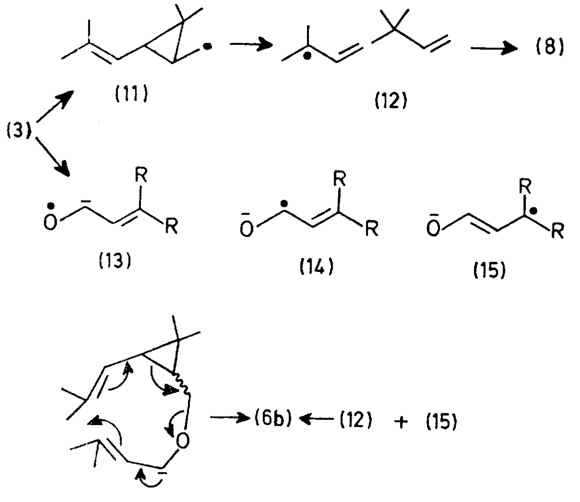

(10)

(a), R = H; (b), R = Me

The allylic alcohol (**4a**) results from 1,2-shift in the allyl ether anion (**3**) whereas (**10a**) is produced as a result of reaction between an excess of Bu^{n}Li and the aldehyde product (**5a**) formed from concomitant 1,4-shift ([1,4] sigmatropic change) in (**3**). In some runs, pure aldehyde (**5a**) could be separated by chromatography. The allylic alcohol (**9a**), the minor product of the reaction, results effectively from a bis-homo-1,6-allylic shift (homo [2,5] sigmatropic change) once again involving the anion (**3**).



Scheme

The hydrocarbon (**8**) is almost certainly produced during a radical dissociation–dimerisation sequence (*viz.* **3** → **11** → **12** → **8**). Indeed it is highly probable that products (**4**), (**9**), and (**10**) are also produced by way of recombination of radicals (**11**) and (**12**) and of radical anions (**13**), (**14**), and (**15**).[3] The origin of chrysanthemyl alcohol (**1**) in the reaction between (**2a**) and $Bu^{n}Li$ is not immediately clear.[1b]

In parallel studies with the corresponding dimethylallyl ether (**2b**) (both *cis*- and *trans*-isomers were examined), significant quantities of the aldehyde (**6b**) (*ca.* 18%) and of the alcohol (**7b**) (*ca.* 12%) produced from ***in situ*** reaction between (**6b**) and $Bu^{n}Li$, were isolated in addition to (**1**) (*ca.* 35—40%), (**4b**) (*ca.* 9—11%), (**8**) (*ca.* 9—10%), and (**9b**) (*ca.* 1—3%). The aldehyde (**6b**) is produced as a result of homo [4,5] sigmatropic rearrangement from the anion (**3b**), and the process can be formulated as shown in the Scheme.[4] An alternative, perhaps more likely, mechanism for the transformation (**3b**) → (**6b**) involves a radical pathway *via* species (**12**) and (**15b**). The two additional methyl groups on the allylic radical (**15b**) apparently stabilise the radical species to such an extent that a homo [4,5] sigmatropic change is favoured in the dimethylallyl ether case.†

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† A similar homo [**4,5**] sigmatropic rearrangement was observed with the corresponding cinnamyl ether derived from (**1**).

[1] (a) U. Schöllkopf, *Angew. Chem. Internat. Edn.*, 1970, **9**, 763: H. Felkin and A. Tambute, *Tetrahedron Letters*, 1969, 821; V. Rautenstrauch, *Chem. Comm.*, 1970, 4; J. E. Baldwin and J. E. Patrick, *J. Amer. Chem. Soc.*, 1971, **93**, 3558; J. F. Garst and C. D. Smith, *ibid.*, 1973, **95**, 6870; V. Rautenstrauch, G. Büchi, and H. Wüest, *ibid.*, 1974, **96**, 2576; P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *ibid.*, 1966, **88**, 78; (b) J. E. Baldwin, J. DeBernardis, and J. E. Patrick, *Tetrahedron Letters*, 1970, 353.

[2] *Cf.* P. T. Lansbury and V. A. Pattison, *J. Amer. Chem. Soc.*, 1962, **84**, 4295.

[3] See W. D. Ollis, M. Rey, I. O. Sutherland, and G. L. Closs, *J.C.S. Chem. Comm.*, 1975, 543, and refs. cited therein.

[4] *Cf.* T. Laird and W. D. Ollis, *J.C.S. Chem. Comm.*, 1973, 658; W. D. Ollis, R. Somanathan, and I. O. Sutherland, *ibid.*, p. 661.