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A CIDNP STUDY OF THE WITTIG REARRANGEMENT OF ALLYLIC ETHERS

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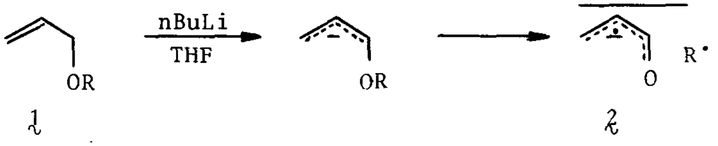
The Wittig rearrangement of allyl alkyl ethers 1 has been shown to lead to a mixture of alcohols 4 and aldehydes 6 arising from [1,2] and [1,4] migration of the alkyl group.[2] This reaction is thought to proceed via a radical + radical-anion cleavage-recombination mechanism (Schemes 1 and 2). It was therefore of interest to examine the products formed in the reaction by nmr to see if radical intermediates could be detected (CIDNP).

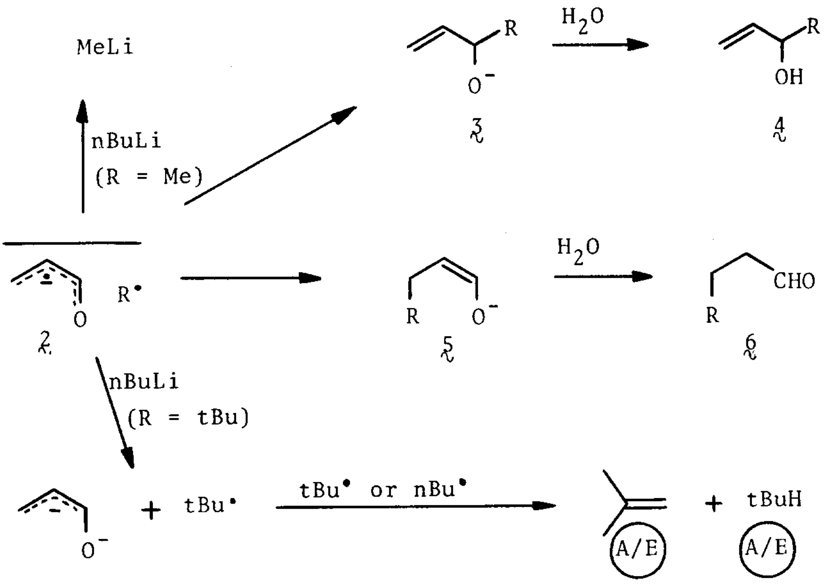


Scheme 1

Lansbury and Chasar[3] observed a polarised signal during the rearrangement of benzyl t-butyl ether; this signal, however, was subsequently found to be due to a by-product, isobutene,[4] rather than to the major rearrangement product.[5]

The rearrangement of the ethers 1 (R = Me and R = tBu) with butyllithium in THF d_8 at 30°C led[6] to a mixture of alkoxides 3 and 5 (Z isomers only,

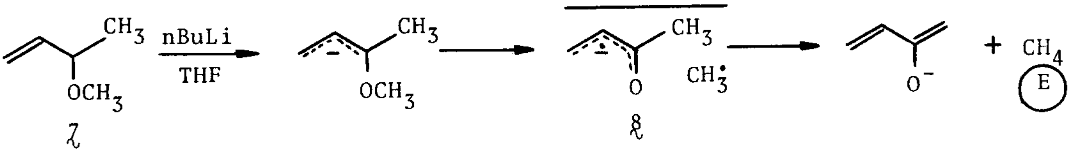
$J_{HC=CH}$ = 8 Hz).[7] No polarisation was observed in these products during the reaction. Three polarised signals (all A/E) were, however, found in the spectrum of the reacting mixture from 1 (R = tBu) at δ = 4.62, 1.69 and 0.89 (doublet). These are attributed to isobutene CH_2 and CH_3, and isobutane CH_3, respectively. Moreover, some unpolarised methyllithium (δ = -2.1) was formed in the reaction of 1 (R = Me).



Scheme 2

The α-substituted allylic ether 7 under the same conditions, led to unpolarised [1,2] and [1,4] rearrangement products (in low yield), unpolarised methyllithium, and polarised methane (E, δ = 0.16).[8]

A variety of polarised by-products have thus been detected in the reaction between butyllithium and allyl alkyl ethers. Polarised methane is only formed from α-substituted methyl ethers such as 7, and probably results from hydrogen transfer within the radical pair 8, as shown in Scheme 3. The fact that the methane exhibits a net E effect shows that there



Scheme 3

is, as expected, a g-factor difference between the two radicals in the pair **8** (-+-- = E).[9, 10] Polarised isobutane and isobutene are formed from **1** (R = tBu), and polarised isobutene has already been observed as a by-product of the Wittig rearrangement of benzyl t-butyl ether.[3, 4] The observed multiplet effect is consistent with a hydrogen transfer reaction between two alkyl radicals ($\Delta g = 0$) as shown in Scheme 2 (+++++- = A/E for isobutane, and ++++-+ = A/E for isobutene).[9, 11]

As in the case of benzyl t-butyl ether,[3] no polarisation was observed in the major rearrangement products **3** and **5** from the allyl alkyl ethers **1**. This is not necessarily inconsistent with a radical process (Schemes 1 and 2) if the first-formed radical pair **2** undergoes immediate recombination.[12, 13] The fact, however, that some racemisation of the migrating group R is observed in the formation of the products **4** and **6** from the ether **1** (R = PhCHMe),[14] shows that part of the reaction occurs by a secondary radical recombination which should therefore lead to polarised products. Polarisation is indeed observed in the products of the analogous Stevens [1,2] rearrangement;[12] these products are, however, neutral molecules, whereas the products **3** and **5** from the Wittig rearrangement are lithium alkoxides. Such alkoxides are known[15] to form large aggregates in solution, and large molecules have short relaxation times T_1. This may be the reason for the lack of observable polarisation in the products of the Wittig rearrangement.[16]

References and footnotes

1. ERA n° 20, CNRS.
2. H. Felkin and A. Tambuté, Tetrahedron Letters, 821 (1969).
3. P.T. Lansbury and D.W. Chasar, unpublished work cited by U. Schöllkopf (ref. 5) and by A.R. Lepley (ref. 4).
4. A.R. Lepley in "Chemically Induced Magnetic Polarisation", Ed. A.R. Lepley and G.L. Closs, Wiley, New York (1973), p. 323.
5. U. Schöllkopf, Angew.Chem.Int.Ed., 9, 763 (1970).
6. The solutions (0.6 mmole nBuLi and 0.3 mmole **1** in 400 μl THF d_8) were prepared at -20°C and transferred to a 100 MHz nmr spectrometer probe, and 22 μsec. 28° pulse spectra [S. Schäublin, A. Höhener and R.R. Ernst, J.Mag.Res., 13, 196 (1974)] were determined at 2 second intervals.

Each free induction decay was stored on tape immediately after it had been accumulated. The spectra were processed (F.T.) after completion of the run. We thank Dr. C. Taïeb for setting up the F.T. programme.

7. The E isomers of **5** (R = Me and tBu) had $J_{HC=CH}$ = 12 Hz.
8. 2-Methoxy $\Delta^{1(9)}$-octalin (mixture of epimers) also gave polarised methane under the same conditions.
9. R. Kaptein, Chem.Comm., 732 (1971).
10. The unpolarised methyllithium formed from the methyl ethers probably arises by electron transfer from excess butyllithium to the methyl moiety of the radical pairs, as shown in Scheme 2 [cf. J.E. Baldwin, J. DeBernardis and J.E. Patrick, Tetrahedron Letters, 353 (1970)]. This process does not occur when R = tBu, since, unlike Me^-, tBu^- is less stable than nBu^-. Some "Wittig" products **3** and **5** (R = nBu) are presumably formed at the same time as methyllithium, and indeed such products were detected (g.c.) in the reaction mixture from **7**.
11. Lepley (ref. 4) has suggested that the isobutene formed from benzyl t-butyl ether arises from the secondary encounter of t-butyl and phenyl ketyl radicals, Δg for this radical pair being assumed to be negligible. This assumption is not consistent with the net effect observed in methane (Scheme 3).
12. U.H. Dolling, G.L. Closs, A.H. Cohen and W.D. Ollis, J.C.S.Chem. Comm., 545 (1975), and refs cited therein.
13. J.F. Garst and C.D. Smith, J.Amer.Chem.Soc., 98, 1526 (1976).
14. H. Felkin and C. Frajerman, preceding paper.
15. C.W. Kamienski and D.H. Lewis, J.Org.Chem., 30, 3498 (1965).
16. We have measured the relaxation times T_1 of the tBu and vinyl protons in the lithium alkoxides **3** and **5** (R = tBu) in THF d_8; they all lie between 0.5 and 1.0 sec. at 22°C.