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1,4-ALKYL SHIFTS IN THE WITTIG REARRANGEMENT OF ALKYL ALLYL ETHERS

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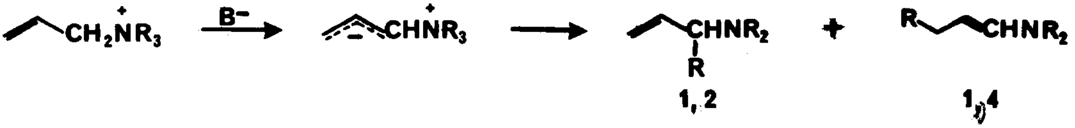
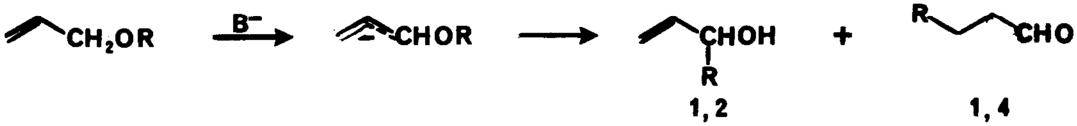
The Stevens rearrangement (1) of allylic quaternary ammonium salts has been shown to lead to a mixture of tertiary amine and enamine, formed through concomitant 1,2- and 1,4-alkyl shifts (2):

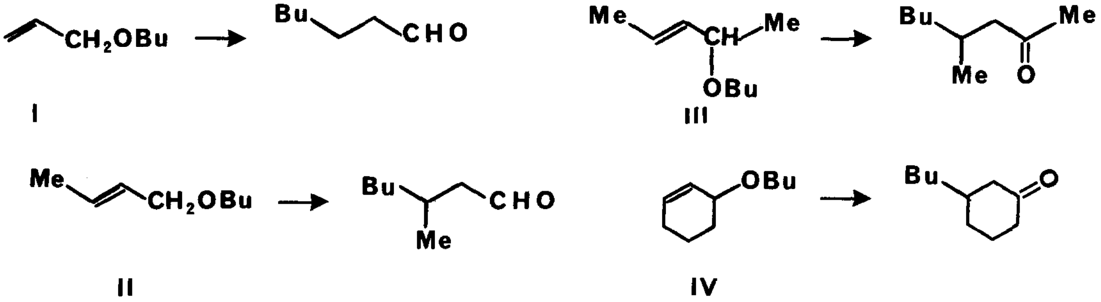


As far as we are aware, only two examples of the analogous Wittig rearrangement (1) of allylic ethers (involving abstraction of the allylic proton) have been reported. Somewhat surprisingly, however, in both cases the only product isolated was the alcohol resulting from a 1,2-shift (3); no carbonyl compound, resulting from a 1,4-shift, appears to have been detected (4):



We have found that, like their quaternary ammonium counterparts, alkyl allyl ethers do in fact undergo a 1,4-alkyl shift when submitted to the conditions of the Wittig rearrangement. The ethers I - IV, when treated with an excess (30%) of an equimolar mixture of propyllithium and NNN'N'-tetramethylethylenediamine (TMEDA) (5) in pentane, all afforded (after quenching with aqueous acid) the aldehydes and ketones shown, in about 30% yield (6). A number of other products were also formed, including the allylic alcohols resulting from a 1,2-alkyl shift; some of these, however, react at a significant rate with the excess propyllithium (7), and the yields ranged from 7% to 33%.

The same rearrangement occurs when tetrahydrofuran (THF) is used instead of TMEDA. Thus, the ether I and propyllithium in a mixture of equal volumes of pentane and THF afforded (after hydrolysis) 29% of heptanal and 23% of hepten-3-ol; small amounts of but-1-ene and hex-1-ene were also detected. In pentane alone, the reaction led to 73% of hex-1-ene (3b), with no more than a trace of the Wittig rearrangement products.



I

III

II

IV

The yields of carbonyl compounds (1,4-alkyl shift) are remarkably insensitive to the substitution pattern in the allylic moiety of the ethers I - IV; this lends further support to the radical + radical-anion cleavage-recombination mechanism (8) for the Wittig rearrangement.

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Footnotes

1. Review: D.J.Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York and London (1965).
2. E.F.Jenny and J.Druey, Angew.Chem., 74, 152 (1962); H.Hellmann and G.M. Scheytt, Ann., 654, 39 (1962).
3. (a) Diallyl ether + potassium amide in liquid ammonia → hexa-1,5-dien-3-ol: C.R.Hauser and S.W.Kantor, J.Amer.Chem.Soc., 73, 1437 (1951). Dicinnamyl ether + butyllithium in THF → 1,4-diphenyl-hexa-1,5-dien-3-ol: G.Wittig and M.Schlosser, unpublished work (1960) [quoted in a footnote by M.Schlosser, J.Organometal.Chem., 8, 9 (1967)]. The Wittig rearrangement of alkyl allyl ethers by butyllithium in ethereal solvents is mentioned, with no details, by (b) C.D.Broaddus, J.Org.Chem., 30, 4131 (1965).
4. This could be because in both cases the migrating group was itself allylic. The Wittig rearrangement of benzyl sec-butyl ether affords traces of p-sec-butyl-benzaldehyde: U.Schöllkopf and W.Fabian, Ann., 642, 1 (1961).
5. G.G.Eberhardt and W.A.Butte, J.Org.Chem., 29, 2928 (1964).
6. The reaction times ranged from 30' at 25° (I) to 17hrs at reflux (IV). The yields were determined by gas chromatography (peak exaltation technique).
7. J.K.Crandall and A.C.Clark, Tetrahedron Letters, in press; H.Felkin, G. Swierczewski, and A.Tambuté, submitted for publication.
8. P.T.Lansbury, V.A.Pattison, J.D.Sidler, and J.B.Bieber, J.Amer.Chem.Soc., 88, 78 (1966); H.Schäfer, U.Schöllkopf, and D.Walter, Tetrahedron Letters, 2809 (1968).