

## Novel Synthesis of Vinyl Ethers induced by Carbon–Halogen Bond Homolysis

Michelle Cook, Owen Hares, Amanda Johns, John A. Murphy,\* and Christopher W. Patterson

*Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.*

Cleavage of 2-aryl-3- $\alpha$ -halogenoalkyloxiranes, brought about by tributylstannyl radicals, leads to products resulting from carbon–carbon bond cleavage.

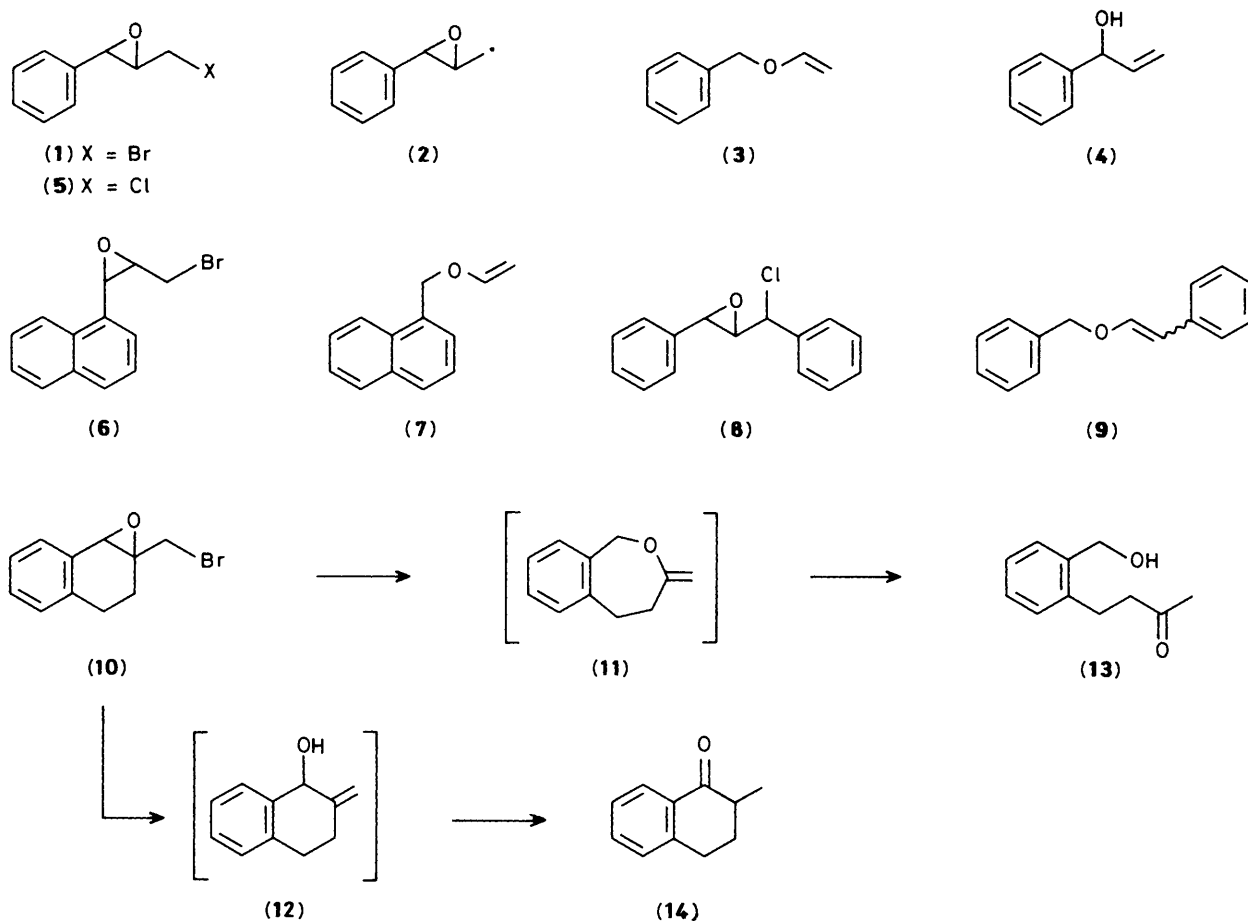
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The utility of radicals in synthesis has recently become apparent.<sup>1</sup> Many of the radical reactions used have involved carbon–carbon bond formation to give either cyclic or acyclic products.<sup>2</sup> Recent mechanistic work in our group suggested that C–C bond cleavage might also be synthetically useful.<sup>3</sup> In the work described below, we have utilized carbon–halogen bond homolysis as a trigger for the cleavage of C–C bonds in oxiranes so producing a novel synthetic route to benzyl vinyl ether and a series of related compounds.

Cleavage of oxirane† (1) by tributylstannyl radicals (generated from tributylstannane and azobisisobutyronitrile) produced the radical (2), which on C–C bond cleavage would ultimately yield (3) and on C–O cleavage would give (4). The vinyl ether (3) was produced as major product (72%) and the

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† All new compounds gave satisfactory spectroscopic data as well as combustion analysis and/or high resolution mass measurement.



allylic alcohol (4) as minor product (24%). The relative yields of these compounds were the same in diethyl ether or tetrahydrofuran. On performing the corresponding reaction on the chloride (5) a very similar ratio of the same products was formed. [The identity of the vinyl ether (3) and the allylic alcohol (4) was confirmed by comparison with samples prepared by other routes.<sup>4</sup>]

Cleavage of the naphthalene derivative (6) on the other hand produced exclusive cleavage to vinyl ether (7) (91%), and likewise the diphenyl compound (8) (a mixture of epimers at the halogen-bearing carbon) gave rise exclusively to vinyl ethers (9) (97%). In an attempt to see whether the same reaction might work in a ring-expanding example, we synthesised the bromide (10). We expected products (11) and (12) from the cleavage of this compound. Instead we isolated compounds (13) (21%) and (14) (5%) following chromatography.

We rationalise (13) as having been produced by silica-catalysed hydration of the desired oxepane derivative (11); the ketone (14) on the other hand was produced during the reaction since the <sup>1</sup>H n.m.r. of the crude reaction mixture indicated the low-field aromatic protons of (14) and the 2,4-dinitrophenylhydrazones of (14) could be isolated on addition of Brady's reagent to the crude product mixture. So we rationalise the production of (14) as the result of an isomerisation of (12).<sup>‡</sup> Although we did not isolate the

oxepane derivative from this reaction, it is clear that C-C bond cleavage has occurred from homolysis of (10). Hence it appears that this cleavage reaction occurs generally for 2-aryl-3- $\alpha$ -halogenoalkyloxiranes. Cleavages of oxiranes which do not feature stabilising groups have been shown to result in breakage of the C-O bond.<sup>5</sup>

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<sup>‡</sup> Although we have not studied the mechanism of this isomerisation, we thank one of the referees for suggesting that a trace of adventitious acid might be responsible for the reaction.