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CONVERSION OF KETONES INTO VINYL-OXIRANES

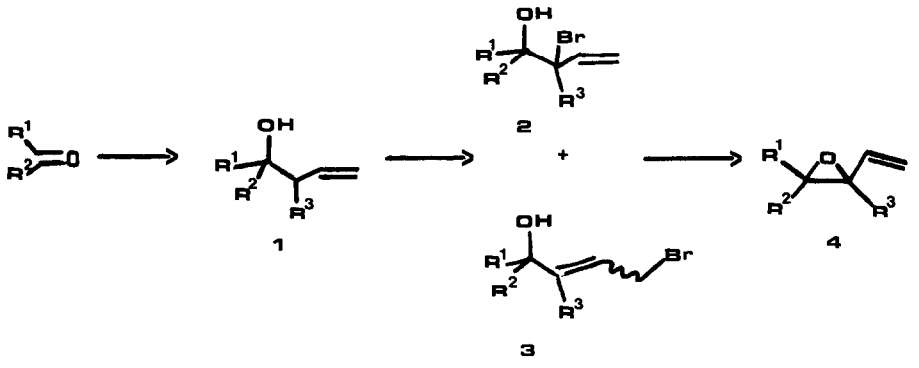
Richard C Cookson* and Robyn L Crumbie

Chemistry Department, The University, Southampton SO9 5NH, U K

Summary : A range of 1-(2-propenyl) alcohols was transformed in good yields into vinyl-oxiranes *via* the allylic bromide.

In connection with another project, we recently found ourselves requiring a series of spiro-oxiranes bearing a vinyl group [4,$R^1R^2=(CH_2)_n$]. Existing methodology for the synthesis of such compounds was sparse. The few examples cited proceeded through intermediate sulfur ylids[1,2] which ring-closed by way of substitution of the alkoxide with consequent extrusion of a sulfide, or by selective epoxidation of a diene.[3] Because of the versatility of vinyl-oxiranes in synthesis we now describe a simple way of making them from ketones.

In order to minimise the use of strong bases and organometallics, which restricted the generality of existing methods, we chose to form various propenyl substituted alcohols and then to introduce a suitable leaving group, enabling subsequent ring closure. The alcohols chosen were synthesised in high yield from Grignard reaction of the appropriate ketone and the allyl-magnesium chloride, the latter readily formed at room temperature from magnesium powder activated by ultrasound. Allylic bromination with N-bromosuccinimide gave the 3-bromo-1-propenyl alcohols (3) from 1-methyl- and 1-phenyl-2-propenyl alcohols and mixtures of the 1-bromo (2) and 3-bromo (3) isomers from the unsubstituted propenyl alcohols (n.m.r. spectroscopy), which were used without purification. Seebach's two-phase system[1] could be used for ring closure, but the method was by no means general



as in many cases only unchanged substrate and polymeric material were recovered. Changes in concentration and use of phase transfer catalysis had no substantial effect. The formation of the alkoxide by stronger bases in a range of organic solvents likewise gave no oxirane products. This was apparently due to the nucleophilicity of the alkoxide being strongly curtailed, by tight interaction with the cation, for use of the appropriate crown ether resulted in internal substitution of alkoxide and loss of bromide to afford the epoxides in high yield. In no case were spirodihydrofurans detected. Initial purification by suction chromatography removed brominated by-products, and the product thus obtained could be easily further purified by distillation or flash chromatography.

A range of oxiranes prepared by this procedure is shown in Table 1.[4] It can be seen that the method can be applied to both linear and cyclic substrates, and it is to be noted that steric hindrance of the tertiary alkoxide (*e.g.* by ring size, or substitution at the β carbon atoms) and its nucleophilic attack at a tertiary centre place no restrictions upon the generality of the reaction under the given conditions.

General Procedure : Synthesis of 2-ethenyl-1-oxaspiro[2.4]heptane[4,$R^1R^2=(CH_2)_4$,R^3=H]

N-Bromosuccinimide (10.7 g, 60 mmol) and a catalytic amount of benzoyl peroxide were added to a solution of 1-(2-propenyl)cyclopentanol (6.3 g, 50 mmol) in carbon tetrachloride (150 ml), and the mixture was irradiated till no unreacted N-bromosuccinimide was apparent and n.m.r. spectroscopy indicated that reaction was complete. The solution was filtered and washed with water (2 x 50 ml) and brine and dried ($MgSO_4$). Removal of the solvent afforded the bromo-alcohol, which was used without further purification.

The bromo-alcohol in tetrahydrofuran (50 ml) was added dropwise to a stirred slurry of sodium hydride (from 2.64 g, 50% dispersion, 55 mmol) in tetrahydrofuran (50 ml) to which 15-crown-5 (2 drops) had been added at $\sim 20^{\circ}$ [5] under argon. The resultant mixture was stirred till thin layer chromatography indicated complete epoxide formation (~12 h), then diluted with water (300 ml) and the product extracted into ether (6 x 100 ml). The ether extracts were washed with water (2 x 50 ml) and brine, dried ($MgSO_4$) and the solvent *carefully* removed. The crude product was purified by rapid suction flash chromatography (petrol), followed by distillation, to give a colourless liquid (5.3 g, 85%), b.p. 50°/15 mm (lit.[1] 80°/22 mm).

TABLE I

ALCOHOL (1)	EPOXIDE (4)	YIELD	B.P.
1-(2-propenyl)cyclopentanol[6]	2-ethenyl-1-oxaspiro[2.4]heptane	85%	50°/15 mm (lit[1] 80°/22 mm)
1-(2-propenyl)cyclohexanol[7]	2-ethenyl-1-oxaspiro[2.5]octane	87%	61°/15 mm (lit[3] 72°/18 mm)
1-(2-propenyl)-2-methyl-cyclohexanol[8]	2-ethenyl-4-methyl-1-oxa-spiro[2.5]octane	89%	52°/15 mm
1-(2-propenyl)-4-methyl-cyclohexanol[9]	2-ethenyl-6-methyl-1-oxa-spiro[2.5]octane	82%	40-50°/15 mm
1-(2-propenyl)-4-*tert*-butyl-cyclohexanol[10]	2-ethenyl-6-*tert*-butyl-1-oxa-spiro[2.5]octane	93%	65-75°/0.5 mm
1-(2-propenyl)cycloheptanol[11]	2-ethenyl-1-oxaspiro[2.6]nonane	87%	85°/15 mm
1-(2-propenyl)cyclododecanol[12]	2-ethenyl-1-oxa-spiro[2.11]tetradecane	88%	100°/0.2 mm
2-hydroxy-2(2-propenyl)-bicyclo[2.2.1]heptane[13]	2,2'-spiro[bicyclo[2.2.1]heptane-3-ethenyloxirane]	62%	70-85°/15 mm
1,1-dimethoxy-2-methyl-4-penten-2-ol	2-(dimethoxymethyl)-2-methyl-3-ethenyloxirane	71%	40°/15 mm
1-(1-methyl-2-propenyl)-cycloheptanol, bp 100°/15 mm	2-ethenyl-2-methyl-1-oxa-spiro[2.6]nonane	89%	40°/15 mm
1-(1-phenyl-2-propenyl)-cyclopentanol, bp 75°/0.3 mm	2-ethenyl-2-phenyl-1-oxa-spiro[2.4]heptane	92%	85°/0.3 mm
1-(1-phenyl-2-propenyl)-cycloheptanol, bp 65°/0.15 mm	2-ethenyl-2-phenyl-1-oxa-spiro[2.6]nonane	93%	85°/0.15 mm
4-ethyl-3-phenyl-1-hexen-4-ol, 47°/0.3 mm	2,2-diethyl-3-ethenyl-3-phenyloxirane	85%	50°/0.2 mm

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4. All new compounds were fully characterised by n.m.r. spectroscopy and analysis and/or accurate mass measurement.

5. NOTE: The reaction is extremely slow at lower temperatures.

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