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1 → 6 OXYGEN TRANSPOSITION OF A CYCLOHEX-2-ENONE

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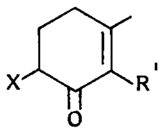
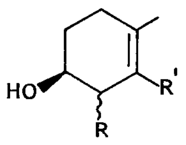
Abstract *The 1 → 6 transposition can be achieved by 6-hydroxylation, reduction to the cis-diol, cyclic carbonate formation, and reduction with sodium cyanoborohydride-tetrakis(triphenylphosphine)palladium(o)-tetrahydrofuran.*

In connection with our work on polyene cyclisation[1] we required a general method for O-transposition typified by the conversion of (1) into (4). As a first step the enone (1) was converted to its TMS enol ether (LDA-Me_3SiCl-THF) and oxidized[2] with m-chloroperbenzoic acid to give, after hydrolysis, the hydroxyketone (2) (80%) δ_H 4.1 (dd, J 13.5 and 6Hz). Reduction of (2) with $LiAlH_4$-$AlCl_3$[3] did not effect hydrogenolysis but gave the cis-diol (5) with high selectivity in contrast to the result with $LiAlH_4$ (Table).[†]

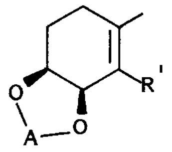
$$R' = (CH_2)_2CH = CHMe$$



1 X = H
2 X = OH
3 X = OAc

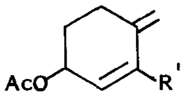


4 R = H
5 R = ◀OH
6 R = ⋯OH

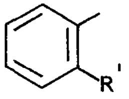


7 A = BPh
8 A = C=O
9 A = C=S

[†] The high stereoselectivity observed in the LAH-$AlCl_3$ reductions is in accord with the formation by coordination of a 5,6-ring system and its preferential reduction to the cis-ring junction.



(10)



(11)

Table. Reduction of hydroxyketone (2)

Reagent	*Yield (%)*	*Ratio* *cis-(5)* : *trans-(6)*[a]
LAH-AlCl$_3$		
1 : 1	95	81 : 19
1 : 2	85	85 : 15
1 : 3	77	83 : 17
1 : 4	88	92 : 8
LAH	95	43 : 57
NaBH$_4$	91	50 : 50
Red-Al^R	90	33 : 67

[a] determined by capillary gas chromatography.

Attention was then turned to the hydrogenolysis of some cyclic derivatives of the *cis*-diol (5). LiAlH$_4$-AlCl$_3$ reduction of the boronate[4] (7) gave unidentified products while similar reduction of the carbonate[5] (8) (N,N'-carbonyldiimidazole, 88%) gave *ca*. 15% of the required alcohol (4) and a similar proportion of diol (5). Although not fully characterised the other products from these reactions appeared to be cyclisation products arising from participation of the side-chain. Not surprisingly reduction of the carbonate (8) with LiAlH$_4$ gave the diol (5) (95%) and the alcohol (4) (2%). A low yield of the alcohol (4) was also obtained by Bu^{n}_{3}SnH reduction[5] of the cyclic thiocarbonate (9)[7] (N,N'-thiocarbonyldiimidazole, 70%).

Allylic phosphate esters, followed by sulphate, are preferred for enhancing allylic hydrogenolysis relative to other reductive processes. However, we were unable to prepare cyclic phosphates or sulphates from the diol (5) and turned to methanesulphonates. Acetylation of the ketol (2) gave the acetate (3), which on NaBH$_4$-MeOH reduction gave an unexpectedly complex mixture of five compounds identified as the *cis*-diol (5) and both *cis*-monoacetates and the *trans*-diol (6) and its homoallylic acetate; the *trans-cis* ratio was 36 : 64. $Zn(BH_4)_2$ in Et_2O reduced the ketone (3) to the expected monoacetates (*trans*:*cis* 90 : 10) as did $NaBH_3CN$-MeOH-HCl. Reaction of this mixture of monoacetates with CH_3SO_2Cl-Et_3N gave elimination products.[‡]

The required allylic deoxygenation was finally achieved using the allylic reduction method described by Hutchins[8] for allylic acetates, *viz* reaction with $NaBH_3CN$-$Pd(PPh_3)_4$-THF. However, this system did not react with the allylic monoacetates, diacetates, or bis-ethylcarbonates of the diols (5) and (6) and the alcohol (4) [δ_H 5.4 (2Hm), 3.9 (1Hm), 1.6 (6H, bs)] was only obtained by reduction of the cyclic carbonate (8) (62%). Presumably, in the former cases, the likely intermediate π-allylpalladium complex is not formed due to the extent of alkylation of the allyl system, whereas when the leaving group is the cyclic carbonate it does form, perhaps encouraged by a relief of steric strain coupled with the possible irreversibility of complex formation due to CO_2 loss. The overall yield of alcohol (4) from enone (1) was 40%.

All compounds reported in the text gave satisfactory accurate mass measurements and/or combustion analyses and consistent n.m.r. spectra.

Acknowledgement

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[‡] Spectroscopic properties support structure (10) [λ_{max} 236 nm; ν_{max} 1740 cm^{-1}; δ_H 5.40 (4H, m), 5.05 (1H, m) and 4.90 (1H, m)] which on storage is converted to (11) [λ_{max} 254 nm; δ_H 7.18 (3H, m), 5.55 (2H, m), 2.34 (3H, s), 1.68 (3H, d)].

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