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REGIOSELECTIVE REDUCTIONS OF 2,3-EPOXY ACETALS WITH ZINC-CHLOROTRIMETHYLSILANE AND LITHIUM ALUMINIUM HYDRIDE: CONVENIENT SYNTHESIS OF 1,2 AND 1,3-DIONES

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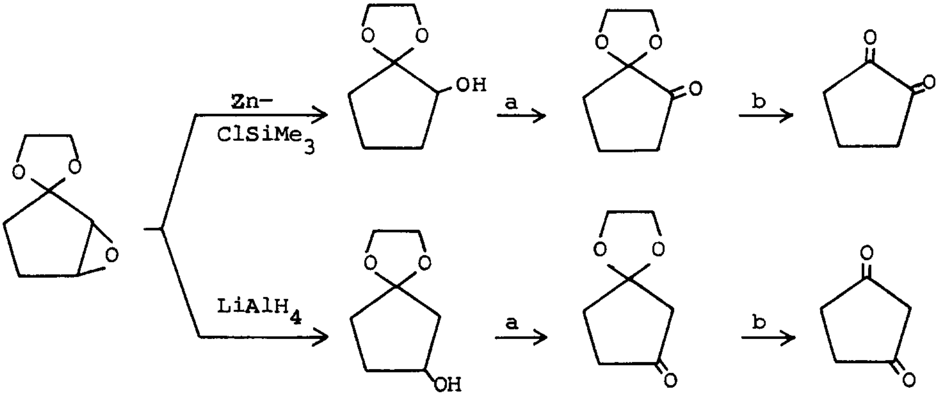
Summary: A variety of 2,3-epoxy acetals have been found to undergo regioselective reductions with zinc-chlorotrimethylsilane and lithium aluminium hydride to give 2-hydroxy and 3-hydroxy acetals respectively. Their oxidation followed by hydrolysis furnished the corresponding 1,2- and 1,3-diones in good yields.

Recently we have reported[1] the use of zinc-chlorotrimethylsilane as a convenient reducing system for the conversion of epoxides into alcohols. It was observed by us that unsymmetrical epoxides yielded the less substituted alcohols as the major product during this reduction. In continuation to further explore the scope[2] of this reducing system we have now found that 2,3-epoxy acetals undergo reduction to yield 2-hydroxy acetals in excellent yields (see table). Their oxidation with pyridine - chromium trioxide resulted into the formation of 2-keto acetals whose hydrolysis furnished 1,2-diones in good yields.



a: Pyridine-CrO_3 b: 15% H_2SO_4

The remarkable regioselectivity in this reduction prompted us to find out the behaviour of these epoxides towards $LiAlH_4$ since it is normally utilised to reduce epoxides. Interestingly, in this case also we have found that these epoxides are regioselectively reduced but to furnish 3-hydroxy acetals instead of 2-hydroxy acetals. Their oxidation to obtain 3-keto acetals followed by hydrolysis furnished 1,3-diones in good yields. The two methods complement each other and should be useful in organic synthesis for the preparation of 1,2 and 1,3-diones from the same substrates. Work is in progress to further extend the scope of these reductions and to assess the mechanistic details responsible for the observed regioselectivities. Epoxy acetals (2 to 5) were prepared by epoxidation of the corresponding olefinic acetals[3] with m-chloroperbenzoic acid. However, the epoxidation of cyclopentenone acetal (cf. entry1) proved to be futile. The epoxide was, therefore, prepared by converting the olefin into the bromohydrin[4] followed by treatment with NaH in THF.

Typical procedures for the preparation of cyclopentane-1,2-dione and cyclopentane-1,3-dione from epoxy acetal 1 are described below:

1. Reduction of 1 with Zn-ClSiMe$_3$

To a stirring suspension of freshly activated zinc dust (588.20 mg, 9 m atom) in dry CH_2Cl_2 (1 ml) was added chlorotrimethylsilane (913 mg, 8.4 mmol) under N_2 atmosphere at 0°C and further stirred for 5 min. A solution of the epoxy acetal 1 (426 mg, 3 mmol) in 1 ml of dry CH_2Cl_2 was then added to this mixture over a period of 10 min. and stirred for 20 min. The reaction mixture was quenched with saturated aq. $NaHCO_3$ solution till neutral and then filtered and the filtrate partitioned into two layers. The aqueous layer was thoroughly extracted with CH_2Cl_2 (3x20 ml) and the combined organic layers were washed with brine (20 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a thick oil whose purification on a column (packed with tlc grade silica gel) afforded pure 2-hydroxy cyclopentanone acetal, 400 mg (92%).

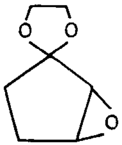
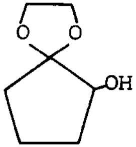
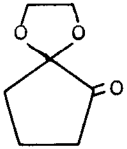
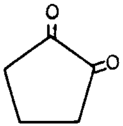
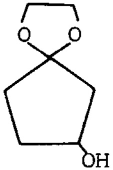
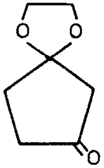
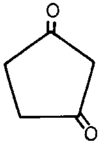
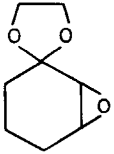
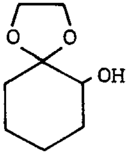
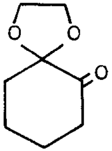
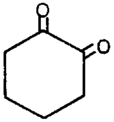
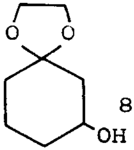
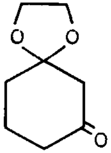
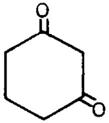
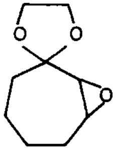
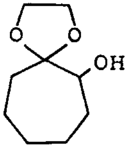
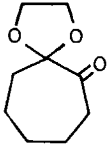
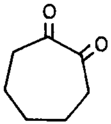
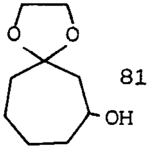
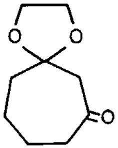
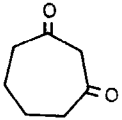
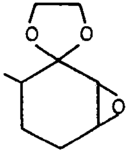
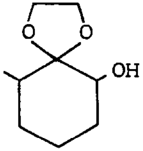
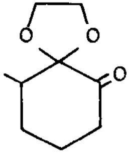
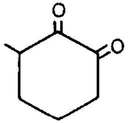
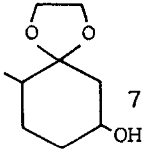
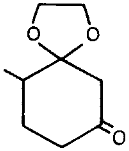
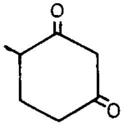
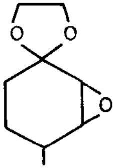
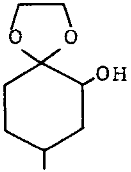
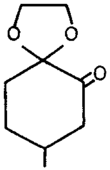
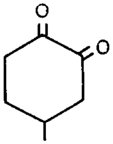
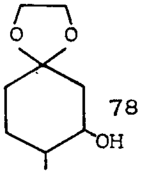
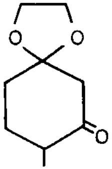
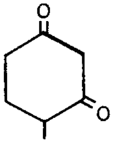
2. Reduction of 1 with LiAlH$_4$

To a slurry of excess of $LiAlH_4$ (600 mg) in dry THF (4 ml) was slowly added a solution of epoxy acetal 1 (426 mg, 3 mmol) in 2 ml THF. The resulting mixture was refluxed for 24 hrs, cooled and then poured into a saturated solution of Rochelle salt. It was then extracted with ether (3x25 ml) after saturating with NaCl. The combined ether layers were washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a residue which was purified by distillation under vacuum to give pure 3-hydroxy cyclopentanone acetal, 350 mg (81%), b.p. 100°C/4 mm.

3. Oxidation of 2-hydroxy and 3-hydroxy cyclopentanone acetals

A solution of dry pyridine (2.37g, 30 mmol), in 25 ml CH_2Cl_2 was treated with chromium trioxide (1.50g, 15 mmol) and dry keiselguhr (1g) at 10-15°C. The mixture was then stirred at room temperature for 20 min. followed by addition of a solution of 2-hydroxy cyclopentanone acetal (216 mg, 1.5 mmol) in 1 ml. CH_2Cl_2 into it. The reaction mixture turned black immediately which

TABLE

Entry	Epoxy Acetal	Zn–ClSiMe$_3$ redn. Pdt^{a,b}	% Yield	Py–CrO$_3$ oxdin. Pdt^b	% Yield	Hydrolysis Pdt^b	% Yield	LiAlH$_4$ redn. Pdt^b	% Yield	Py–CrO$_3$ oxidn. Pdt^b	% Yield	Hydrolysis Pdt^b	% Yield
1			92		75		73		81		85		61
2			90		80		63		86		90		60
3			93		77		79		81		78		71
4			93		72		65		73		71		68
5			93		75		79		78		71		71

a: Distillation led to substantial decomposition in all cases, and hence purified by column chromatography

b: All the compounds gave satisfactory physical and spectral data.

was stirred for additional 20 min. Dilution of the reaction mixture with anhydrous ether (25 ml), filtration through a pad of keiselguhr and tlc grade silica gel was then done. The silica cake was thoroughly washed with ether and the combined filtrate concentrated under vacuum to obtain a thick oil whose purification on a column (packed with tlc grade silica gel) yielded pure 2-keto cyclopentanone acetal (100 mg, 75%). Oxidation of 3-hydroxy cyclopentanone acetal (144 mg) (cf. exptl. no.2), as described, above gave 3-keto cyclopentanone acetal 120 mg (85%).

4. Hydrolysis of 2-keto and 3-keto cyclopentanone acetals

To a suspension of silica gel (column chromatographic grade, 100-200 mesh, 400 mg) in CH_2Cl_2 (2 ml) was added 15% H_2SO_4 (0.1 ml). The mixture was stirred until the turbidity in the CH_2Cl_2 layer had disappeared. A solution of 2-keto cyclopentanone acetal (120 mg, 0.85 mmol) in CH_2Cl_2 (1 ml) was added to the reaction mixture and stirred for 24 hrs at room temperature. The reaction mixture was treated with $NaHCO_3$ until neutral and then filtered and washed the residue with CH_2Cl_2. The combined organic layer was concentrated to obtain a thick liquid which was purified by thick layer chromatography to obtain pure cyclopentane-1,2-dione (60 mg, 73%) m.p. 52°C (Lit^5 mp. 55-6°C).

Hydrolysis, as above, of 3-keto cyclopentanone acetal (71 mg, 0.5 mmol) gave 30 mg (61%) of cyclopentane-1,3-dione, mp. 148°C (Lit^6 mp. 151-2°C).

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