DARZENS CONDENSATION FOR STEREOCONTROL IN SUGAR TEMPLATE

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During the course of the synthetic studies on asymmetric induction from sugar template, we found that Darzens condensation effected high stereocontrol in unsymmetrically substituted cyclic ketones (1 and 5). Treatment of 5a with chloroacetate in the presence of NaOEt afforded the glycidic ester 6a and 7a [80 : 20]; while the same reaction with $LiN(TMS)_2$ as base gave them in 93 : 7. Similarly, 5b [R=i-Pr] gave exclusively 6b [100 : 0]. The method was applied to 1,6-anhydrosugar (1), which was treated under the similar condition to produce a single product 3. The stereochemistry of 3 was assigned as above cases; while the stereochemistry at the 3-position of 3 was determined by converting 1 into a cyclic carbonate (4).