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BORANE REACTIONS X[1]: PREPARATION OF TRANS-1,2-DIOLS BY THE HYDROBORATION OF ENOLATES AND ENOL-TRIMETHYLSILYL ETHERS.

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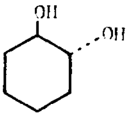
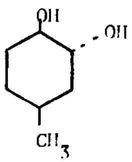
We have shown recently[2] that hydroboration of allyl-lithium compounds lead, after oxidation, to 1,3-diols. We have now found that hydroboration-oxidation of sodium or lithium enolates gives trans-1,2-diols.

The sodium enolate of cyclohexanone, prepared[3,4] by heating the ketone with sodium hydride in 1,2-dimethoxyethane, was treated with a solution of borane (3 moles) in tetrahydrofuran in an ice bath for 2 hours. Oxidation[5] with alkaline hydrogen peroxide gave trans-1,2-cyclohexandiol (I) in a 45% yield (distillation). The same reaction with the sodium enolate of 4-methylcyclohexanone led to a mixture of the trans-diols II and III (combined yield: 55%, TLC) in a 3:2 ratio[6]. A similar 3:2 ratio[7] of the trans-diols IV and V (combined yield: 45%, TLC) was obtained from 4-phenylcyclohexanone.



I



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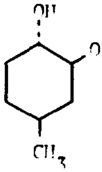

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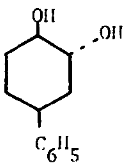

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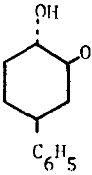
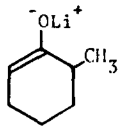


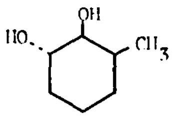
V

The same ratio of similar isomers obtained in the last two reactions proves that steric effects of the substituents in the ring do not determine the course of the hydroboration and that both enolates react essentially from the same conformation with the substituent in the equatorial position. This ratio also supports the view that the hydroboration transition state has a structure similar to that of the olefin[8]. There is only a low preference for attack of borane on one side over attack on the other side of the double bond, through a chair-like or boat-like transition state[8] respectively.

The methods known[3,4] to give separately, under different conditions, one of two possible enolates from the same ketone have been used to prepare different sets of isomeric diols from the same starting material. Thus treatment of 2-methylcyclohexanone with triphenylmethyl-lithium[9] gave the kinetic product VI. The hydroboration-oxidation of VI gave in 70% yield (distillation) a mixture of the trans-diols VII and VIII in a ratio of 42:58[10] (traces of X were also detected).



VI



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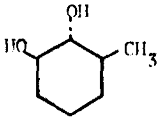
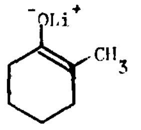


VIII



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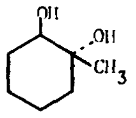
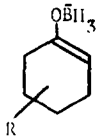
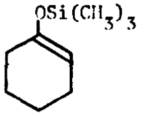


X

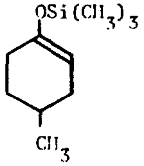
On the other hand the enolate IX, obtained by the isomerization of VI in the presence of excess starting ketone[9], gave the trans-diol X in a 60% yield[12,13] (distillation). It was accompanied by small amounts of VII and VIII derived from VI. The ratio of VII and VIII (2:3), was different from the ratio of II and III (3:2). This ratio was probably determined by the eclipsing interaction, in the transition state resulting from VI, between the oxygen and methyl during the attack of borane trans to the methyl. Monoalcohols were also formed in all the above reactions, but their composition was not analyzed.



XI



XII



XIII

The first position of borane attack on an enolate was probably on the oxygen, because the charge is concentrated mostly on this atom and also due to the high affinity of boron for oxygen. The formed borate XI was attacked by boron preferentially on the olefinic carbon that was not linked to oxygen, even when this carbon was substituted with a methyl as in IX.

Hydroboration-oxidation was also performed on the trimethylsilyl ethers XII and XIII derived from the enolates of cyclohexanone and 4-methylcylohexanone by treatment with trimethylchlorosilane[4]. The ether XII gave 70% of I and XIII gave 65% (TLC) of II and III in a 38:62 ratio[6].

This ratio, which is different to that in the product mixture from the hydroboration of the corresponding enolate, reflects the interaction of borane with the axial hydrogen at position 4 which is pushed towards the double bond by the geminal methyl. This steric effect becomes more pronounced in the hydroboration of XIII than in XI, because of the cooperative action of the methyl and trimethylsilyl groups. The enol trimethylsilyl ethers are therefore useful intermediates, since the yields of diols in their hydroboration are higher and the ratio of products are different than in the case of the enolates.

The hydroboration of ketone derivatives, such as enol acetates,[14-17] enol ethers[17,18] and enamines[19,20] was previously studied. Diols were obtained in similar yields to ours and were also accompanied by monoalcohols. Our method is simpler, since it is a one-pot procedure starting from a ketone and it permits easy access to isomeric diols by controlling the direction of enolate formation.

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6) Determined by GLC using authentic II (prepared by trans-hydroxylation of 4-methylcyclohexene) and III (isolated from the hydroboration of 5-methyl-1,3-cyclohexandione according to reference 1).

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10) Determined by GLC by comparison with authentic VII and VIII[11].

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12) The yield is approximate as it was based on the amount of methyl lithium used to prepare triphenylmethyl lithium. Diol X was identified by comparison with an authentic sample, prepared by *trans*-hydroxylation of 1-methylcyclohexene.

13) All the diols were identified by comparison of their NMR spectra with those of authentic materials.

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