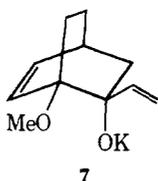


Figure 1. Effect of 18-crown-6 on the rate of rearrangement of **2a** ($M = K$) in THF at 0° .

conditions which **2a** ($M = K$) rearranges within minutes (66° , THF) the diene **7** shows no rearrangement even after heating for 24 hr.



Both the increased yields and lower reaction temperatures encountered in these anionic oxy-Cope processes imply that these modifications should significantly improve the synthetic utility of these and related molecular rearrangements. The full scope of these modified sigmatropic processes will be reported in due course.

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Reduction by a Model of NAD(P)H. Effect of Metal Ion and Stereochemistry on the Reduction of α -Keto Esters by 1,4-Dihyronicotinamide Derivatives

Sir:

Stereospecific reduction of pyruvate to D- or L-lactate by the reduced pyridine nucleotide, NADH, is catalyzed by a D- or L-lactate dehydrogenase, respectively.¹⁻³ To help understand the mechanism of biochemical processes,⁴ we have constructed and studied a model system⁵ whose reduction proceeds stereoselectively under mild conditions and which, therefore, may also be used in organic syntheses.

In this communication, we wish to report mild and stereoselective nonenzymatic reduction of esters of pyruvic acid⁶ and benzoylformic acid^{6,7} in the presence of magnesium perchlorate or zinc perchlorate and a 1,4-dihyronicotinamide derivative, a model of NAD(P)H. Stereoselective reduction by a model of NAD(P)H has not previously been reported. The reaction may be valuable in determining the mechanism of biochemical coenzyme-substrate interaction.

Ethyl benzoylformate in acetonitrile is not reduced by 1-benzyl-1,4-dihyronicotinamide (BNAH) alone at room temperature in the dark.⁸ In the presence of an equimolar amount of magnesium perchlorate, however, ethyl benzoylformate was converted into racemic ethyl mandelate quantitatively. A mixture of 1 mmol each of ethyl benzoylformate, BNAH, and magnesium perchlorate in 15 ml of acetonitrile was allowed to react for 17 hr at room temperature; 5 ml of water was then added. The mixture was concentrated in vacuo and the residual oil was column-chromatographed on silica gel and eluted with benzene or ethanol. Recovered ethyl benzoylformate, ethyl mandelate, and 1-benzyl-3-carbamoylpyridinium perchlorate ($\text{BNA}^+\text{ClO}_4^-$) were identified from their spectra which were compared with those of authentic samples. The reaction was not affected by hydroquinone (0.5 mmol). Under the same reac-