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Biphenyl Inhibits Stereomutation in Semihydrogenation of 4-Arylbut-2-yn-1-ols

Graham G. Pegg[A,B] *and George V. Meehan*[C]

[A] Department of Chemistry, University College of Central Queensland, Rockhampton, Qld. 4702.
[B] Author to whom correspondence should be addressed.
[C] Department of Chemistry and Biochemistry, James Cook University of North Queensland, Townsville, Qld. 4811.

Abstract

Semihydrogenation of 4-arylbut-2-yn-1-ols in the presence of a quinoline-deactivated palladium catalyst yielded mixtures of (*Z*)- and (*E*)-4-arylbut-2-en-1-ols. We find that stereomutation of the initially formed (*Z*)-alkene product is prevented if biphenyl (10% of the weight of the alkyne substrate) is included in the reaction mixture.

Introduction

As part of our efforts to synthesize vinylcyclopropane substrates for mechanistic studies of sigmatropic hydrogen migrations,[1,2] we needed to effect the stereospecific semihydrogenation of a series of 4-arylbut-2-yn-1-ols. For structurally similar systems, Tedeschi and Clark[3] reported problems with overreduction when palladium catalysts were used on a variety of common supports. These workers found that the addition of powdered potassium hydroxide (up to twice the weight of the palladium catalyst) gave improved alkene yields and eliminated their overreduction problem. Rose and Taylor[4] still reported overreduction (*c.* 10%) in the attempted semihydrogenation of 4-phenylbut-2-yn-1-ol by this method. We report that medium-pressure hydrogenation of this compound with use of palladium supported on barium sulfate and in the presence of the recommended amount of potassium hydroxide[3] yielded (*Z*)-4-phenylbut-2-en-1-ol[4] in 79% distilled yield with no evidence of overreduction. However, the reaction often required external heating or further small additions of catalyst before hydrogen uptake would commence. The reaction time needed to effect the semihydrogenation was therefore impossible to predict and regular monitoring by ^{1}H n.m.r. or g.l.c. was necessary.

Biphenyl Inhibits Stereomutation

Because of the capricious nature of the potassium-hydroxide-deactivated system, we investigated the use of quinoline as an alternative reagent for

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deactivation[5] of the palladium on barium sulfate catalyst. However, both medium-pressure and atmospheric-pressure hydrogenations of 4-phenylbut-2-yn-1-ol with a 1 : 1 weight ratio of the catalyst and quinoline (and both 6% by weight of the substrate) gave a mixture of stereoisomeric 4-phenylbut-2-en-1-ol products. As reported by Rose and Taylor,[4] the ^{1}H n.m.r. spectra of the (*Z*) and (*E*) isomers of the product are distinguishable by the significant chemical shift difference for the allylic methylene doublet centred at δ 4·25 and 4·06 respectively. Integration of these resonances allowed a direct estimation of the (*Z*)/(*E*) ratio. By this analytical method, the medium-pressure and atmospheric-pressure semihydrogenations yielded (*Z*)/(*E*) ratios of 2 : 1 and 3 : 2 respectively.

The stereomutation of initially formed (*Z*)-alkene products has been well documented.[6] Isomerization of a (*Z*)-alkene does not occur over palladium catalyst alone, but the process becomes rapid in the presence of hydrogen.[7] Raphael[8] has investigated product isomerization in the semihydrogenation of oct-4-yne using a variety of common palladium-based hydrogenation catalysts, and the problem is related to the intrinsic activity of the catalyst. Although the classic Lindlar catalyst[9] seems the reagent of choice, 4–10% of the (*E*)-alkene isomer is still a common observation.[8,10]

We now report that the addition of biphenyl (10% of the weight of the alkyne substrate) to the palladium/quinoline catalyst system completely inhibits product isomerization in the semihydrogenation of 4-phenylbut-2-yn-1-ol but does not adversely affect the rate of the semihydrogenation process (typically 15–20 min for completion). Furthermore, the use of biphenyl as the deactivating agent offers considerable practical advantages over the potassium hydroxide system.[3] The reduction process commences more readily and the method is applicable to base-sensitive compounds. Isolation of the alkene free of biphenyl can be achieved by either vacuum distillation or column chromatography. The method has been used for the stereospecific preparation of (*Z*)-4-(4-methylphenyl)but-2-en-1-ol and (*Z*)-4-(4-methoxyphenyl)but-2-en-1-ol.

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