Regio- and stereoselective dimerization of phenylacetylene to (Z)-1,4-diphenylbut-1-en-3-yne over potassium amide loaded on alumina

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Potassium amide loaded on alumina catalyzes the regio- and stereoselective dimerization of phenylacetylene to (Z)-1,4-diphenylbut-1-en-3-yne, the selectivity being 96% at 98% conversion of phenylacetylene.

Keywords: potassium amide, alumina, regio- and stereoselective dimerization, phenylacetylene

1. Introduction

Enynes are important molecules as precursors for building blocks for further structural elaborations. Conjugated enynes can be prepared by dimerization of 1-alkynes in the presence of transition metal catalysts [1–12], dehydration of prop-2-ynyl alcohols [13] or elimination of propargylic carbonates [14].

The dimerization of 1-alkynes is usually performed with the use of transition metal catalysts. The dimerization of 1-alkynes could afford three types of isomer. The head-to-tail dimerization gives 2,4-substituted buten-1-en-3-ynes, while the head-to-head dimerization gives (E)- and (Z)-1,4-substituted but-1-en-3-ynes. Cumulene derivatives are also obtained.

The selectivity of the dimerization depends on the transition metal complexes, the reactant and the reaction conditions [1–12]. (μ-C₅H₅)TiCl₂/i-PrMgBr showed exclusively high catalytic activities for the dimerization of various 1-alkynes to give the head-to-tail bound dimers regioselectively [1]. Pd [2], Zr [3] and Y [4,5] complexes also catalyze the regioselective dimerization to 2,4-disubstituted but-1-en-3-ynes. The dimerization of ethynylsilanes by Pd or Rh complexes produces exclusively (E)-1,4-disubstituted enynes [6,7]. The catalyst (Ir(biPh)PMe₃)₂Cl) promotes the head-to-head dimerization of 1-alkynes, but the ratio of Z to E of the products depends on the reaction conditions [8]. Ru(II) complexes catalyze the regio- and stereoselective dimerization of phenylacetylene to (Z)-1,4-diphenylbut-1-en-3-yne [10]. Ruthenium complexes such as Ru(cod)(cot) (cod = 1,5-cyclooctadiene, cot = cyclooctatriene) catalyze the dimerization of tert-butylacetylene to (Z)-1,4-di-tert-butylbutatriene [12].

The base-catalyzed dimerization of phenylacetylene was first reported by Malkhasyan et al. [15]. They found that phenylacetylene reacts in the presence of metallic sodium in aprotic polar solvents to give 1,3-diphenylbut-1-en-3-yne and diphenylbut-1,3-diyne. Later, Trofimov et al. further demonstrated that stirring of phenylacetylene with KOH–DMSO suspension in a ball-mill at room temperature for 1 h gave essentially a mixture of E and Z isomers of 1,4-diphenylbut-1-en-3-yne in the ratio of 6:1 [16]. On the other hand, it has been reported that phenylacetylene polymerizes in the presence of sodium amide and phase transfer catalysts [17].

Here, we wish to report that potassium amide supported on alumina catalyzes the regio- and stereoselective dimerization of phenylacetylene into (Z)-1,4-diphenylbut-1-en-3-yne.

2. Experimental

Phenylacetylene was purchased from Wako Pure Chemicals and purified by distillation at reduced pressure before use. The purity of phenylacetylene was 99.9% as determined by gas chromatography.

The catalysts, KNH₂ loaded on Al₂O₃ (surface area: 124 m² g⁻¹, average pore diameter: 15 nm) were prepared in an ammoniacal solution of metallic potassium by an impregnation method as follows. Al₂O₃ (0.25 g) was heated in a quartz reactor under vacuum at 773 K
for 3 h. A piece of potassium metal was then introduced to the reactor under nitrogen together with a piece of Fe$_2$O$_3$, which served as a catalyst for the formation of amide [18]. The amount of potassium was 10 wt% as K metal. After evacuating the system to $10^{-3}$ Pa at room temperature, ammonia was liquefied into the reactor cooled with dry-ice-ethanol, in order to dissolve the metal. A blue color due to salivated electrons developed. The blue color gradually faded and disappeared, indicating the transformation of the metal into the amide. The solution was kept in contact with alumina for 1 h and then warmed up to room temperature to pump out most of the ammonia. The system was further heated under vacuum at 573 K for 1 h. The catalyst thus prepared is denoted as KNH$_2$/Al$_2$O$_3$. KNH$_2$ catalysts supported on an oxide other than Al$_2$O$_3$ or activated carbon were prepared in a similar manner. Eu and Yb supported on alumina were prepared also by impregnation of their ammoniacal solutions. These catalysts will be denoted as Eu(liq. NH$_3$)/Al$_2$O$_3$ and Yb(liq. NH$_3$)/Al$_2$O$_3$, respectively. Baba et al. showed that Eu or Yb supported on Y-zeolites exhibits basic character in a similar way and that the active species may be amide or imide type species of the metal [19–21].

CaO and MgO were prepared by heating CaCO$_3$ and Mg(OH)$_2$ under vacuum for 3 h at 998 and 773 K, respectively.

The reactions were carried out at 363 K in the quartz reactor without solvent. Phenylacetylene was introduced into the reactor from its side-arm without exposing the catalyst to air, after the catalyst was prepared. The products were identified with $^1$H NMR and GC-MS. The conversion of phenylacetylene and the yields of the products were determined with a gas-chromatograph (an OV 101 glass column) using propylbenzene as an internal standard.

3. Results and discussion

The reaction of phenylacetylene was carried out with various solid-base catalysts at 363 K for 5 h. Only head-to-head dimerization occurred to yield (Z)- and (E)-1,4-diphenylbut-1-en-3-yne. The yield of the dimers depend greatly on the catalysts, as shown in table 1. Alumina and magnesium oxide showed low activities, while calcium oxide showed some activity. Yb(liq. NH$_3$)/Al$_2$O$_3$ and Eu(liq. NH$_3$)/Al$_2$O$_3$ showed also some activity.

KNH$_2$/Al$_2$O$_3$ showed the highest activity. The selection of the support is crucial; KNH$_2$ supported on oxide other than Al$_2$O$_3$ or KNH$_2$ supported on activated carbon showed very low activities. A pronounced effect of the support has also been observed in the isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene [22]. The Z/E ratio of the products also depends on the kind of catalyst. KNH$_2$/Al$_2$O$_3$ showed a very high stereoselectivity with Z/E ratio of 96/4.

![Figure 1](image-url)