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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.

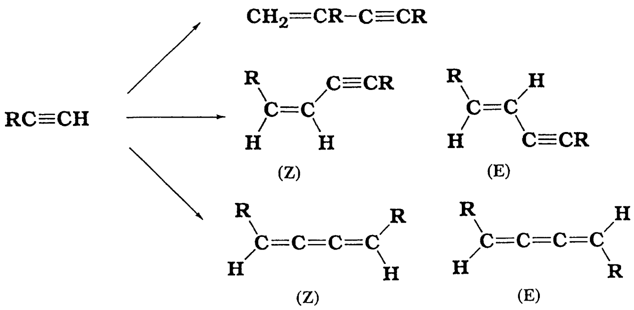
Keywords: potassium amide, alumina, regio- and stereoselective dimerization, phenylacetylene

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-C_5H_5)$TiCl_2$/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-yne. The dimerization of ethynylsilanes by Pd or Rh complexes produces exclusively (E)-1,4-disubstituted enynes [6,7]. The catalyst (Ir(biPh)PMe_3)$_3$Cl) 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, KNH_2 loaded on Al_2O_3 (surface area: 124 m^2 g^{-1}, average pore diameter: 15 nm) were prepared in an ammoniacal solution of metallic potassium by an impregnation method as follows. Al_2O_3 (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_2O_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_2O_3. KNH_2 catalysts supported on an oxide other than Al_2O_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_2O_3 and Yb(liq. NH_3)/Al_2O_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 ^1H 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_2O_3 and Eu(liq. NH_3)/Al_2O_3 showed also some activity.

KNH_2/Al_2O_3 showed the highest activity. The selection of the support is crucial; KNH_2 supported on oxide other than Al_2O_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_2O_3 showed a very high stereoselectivity with Z/E ratio of 96/4.

Table 1

Dimerization of phenylacetylene over various solid-base catalysts at 363 K for 5 h[a]

Catalyst	Yield[b] (%)	Ratio of (Z)/(E) isomers
KNH_2/Al_2O_3	53	96/4
KNH_2/TiO_2	0.4	98/2
KNH_2/activated carbon	0.2	87/13
KNH_2/SiO_2	0.04	75/25
Yb(liq. NH_3)/Al_2O_3	16	70/30
Eu(liq. NH_3)/Al_2O_3	7	62/38
CaO	21	57/43
MgO	4	62/38
Al_2O_3	2	55/45

[a] Reaction conditions: phenylacetylene = 27 mmol, KNH_2/Al_2O_3 0.25 g (K: 10 wt%).

[b] Yield of (Z)- and (E)-1,4-diphenylbut-1-en-3-yne.

When the reactant changed phenylacetylene to 1-hexyne, the isomerization occurred mainly over KNH_2/Al_2O_3. 1-hexyne (27 mmol) was almost converted to 2-hexyne (yield: 86%) when the reaction was carried out at 363 K for 20 h. The other products were not clearly identified by ^1H NMR and GC-MS.

Figure 1 shows the effect of the reaction temperature on the yield and the Z/E ratio of the dimers in the reaction of phenylacetylene over KNH_2/Al_2O_3 for 20 h. The yield of the dimers increased with the reaction temperature. It was 14, 43, and 98% at 313, 348 and 363 K, respectively. At 313 K, the Z-isomer was exclusively

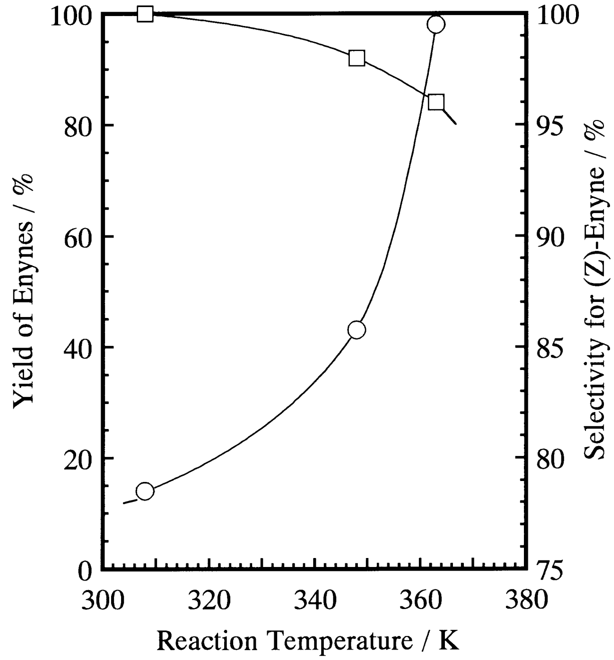
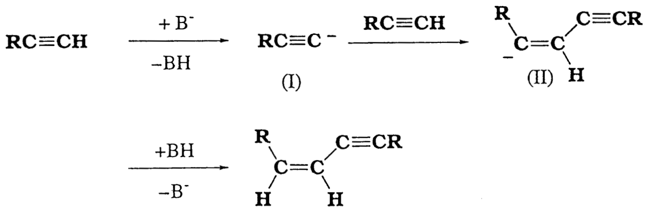


Figure 1. Influence of the reaction temperature on the yield of (Z)- and (E)-1,4-diphenylbut-1-en-3-yne (○) and the selectivity to (Z)-1,4-diphenylbut-1-en-3-yne (□). Reaction conditions: phenylacetylene 27 mmol, KNH_2/Al_2O_3 0.25 g (K: 10 wt%).

formed. The selectivity slightly decreased at higher temperatures.

Figure 2 shows the change in the yield of the dimers with reaction time at 363 K. The yield increased with reaction time and reached 98% at 20 h. Figure 3 shows the change in the selectivity for Z and E isomers as a function of the conversion of phenylacetylene. The selectivity was almost independent of the phenylacetylene conversion. This indicates that the two isomers are formed in parallel and the isomerization of (Z)- to (E)-isomer, the thermally more stable isomer, is slow. However, the Z/E ratio of the products decreased from 96/4 to 27/73 when the reaction time was extended from 20 to 38 h. The conversions of phenylacetylene were 96 and 100%, respectively. This shows that the isomerization of Z- to E-isomer proceeds when phenylacetylene is completely consumed.

We have reported that KNH_2/Al_2O_3 is a very strong base and has an extremely high activity for isomerization of alkenes [22]. Since alkynes are more acidic than alkenes, the dimerization plausibly proceeds through the formation of an acetylide-type intermediate:



The predominance of head-to-head over head-to-tail dimerization is probably caused by the severe steric repulsion between the acetylide (I) and phenylacetylene in the case of head-to-tail dimerization. The high stereoselectivity is also caused by the stability of the Z-type intermediate (II) over the corresponding E-type intermediate because of the steric repulsion between the bulky substituents and the solid surface in the latter case.

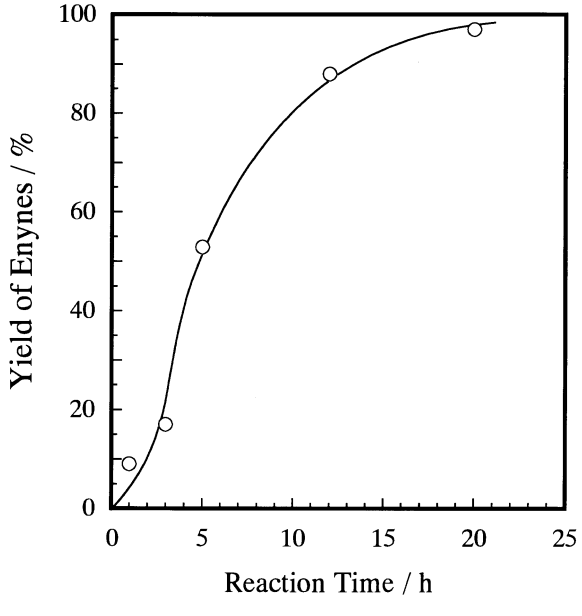


Figure 2. The yield of (Z)- and (E)-1,4-diphenylbut-1-en-3-yne plotted against reaction time. Reaction conditions: reaction temperature 363 K, phenylacetylene 27 mmol, KNH_2/Al_2O_3 0.25 g (K: 10 wt%).

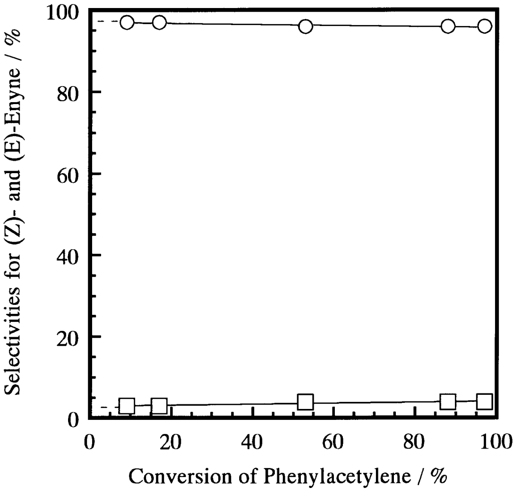
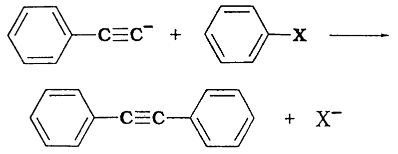


Figure 3. The relation between the conversion of phenylacetylene and the selectivity of (Z)-1,4-diphenylbut-1-en-3-yne (○) and (E)-1,4-diphenylbut-1-en-3-yne (□) at 363 K. Reaction conditions: see figure 2.

The intermediacy of acetylide (I) is supported by the fact that diphenylacetylene was formed when a mixture of phenylacetylene and phenyl chloride (or bromide) was heated with KNH_2/Al_2O_3 at 363 K for 16 h:



In conclusion, this work demonstrates that KNH_2/Al_2O_3 is an efficient catalyst for regio- and stereoselective dimerization of phenylacetylene to 1,4-diphenylbut-1-en-3-yne.

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