

Pd-Catalyzed Telomerization of 1,3-Dienes with Multifunctional Renewable Substrates: Versatile Routes for the Valorization of Biomass-Derived Platform Molecules

Pieter C. A. Bruijninx, Robin Jastrzebski, Peter J. C. Hausoul,
Robertus J. M. Klein Gebbink, and Bert M. Weckhuysen

Abstract The dimerization of 1,3-dienes (e.g. butadiene) with the addition of a protic nucleophile (e.g. methanol) yields 2,7-octadienyl ethers in the so-called telomerization reaction. This reaction is most efficiently catalyzed by homogeneous palladium complexes. The field has experienced a renaissance in recent years as many of the platform molecules that can be renewably obtained from biomass are well-suited to act as multifunctional nucleophiles in this reaction. In addition, the process adheres to many of the principles of green chemistry, given that the reaction is 100% atom efficient and produces little waste. The telomerization reaction thus provides a versatile route for the production of valuable bulk and specialty chemicals that are (at least partly) green and renewable. The use of various multifunctional substrates that can be obtained from biomass is covered in this review, as well as mechanistic aspects of the telomerization reaction.

Keywords Biomass • Butadiene • Oxygenates • Palladium • Telomerization

P.C.A. Bruijninx (✉) • R. Jastrzebski • B.M. Weckhuysen (✉)
Inorganic Chemistry and Catalysis Group, Debye Institute for Nanomaterials Science,
Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands
e-mail: p.c.a.bruijninx@uu.nl; b.m.weckhuysen@uu.nl

P.J.C. Hausoul
Inorganic Chemistry and Catalysis Group, Debye Institute for Nanomaterials Science,
Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

Organic Chemistry and Catalysis Group, Debye Institute for Nanomaterials Science,
Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

R.J.M. Klein Gebbink
Organic Chemistry and Catalysis Group, Debye Institute for Nanomaterials Science,
Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

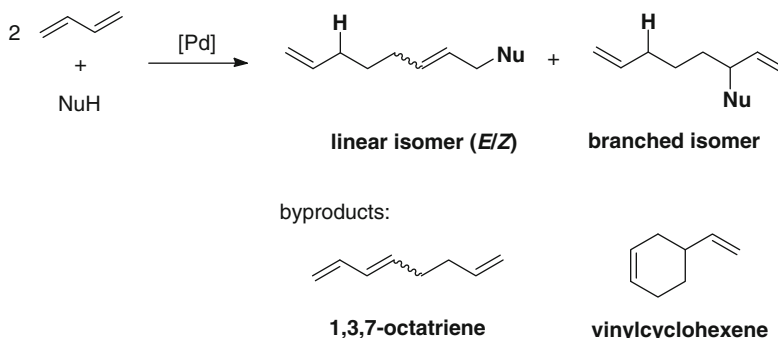
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1 Introduction

The term telomerization is used to describe different processes in different fields of chemistry. The IUPAC compendium, for instance, lists telomerization as “the formation of an addition oligomer, . . . , by a chain reaction in which a chain transfer limits the length of the polymer (‘telomer’) produced”. In the context of homogeneous catalysis, telomerization instead refers to the dimerization or oligomerization of 1,3-dienes with addition of a nucleophile NuH. The nucleophile, or *telogen*, can be any nucleophilic compound as long as it has an “acidic” proton. The number of telogens used is therefore extensive and includes water, alcohols, phenols, amines, silanes, malonates, etc. The other component of the reaction is the 1,3-diene, the *taxogen* and most commonly 1,3-butadiene. The reaction can be catalyzed by various transition metals, including nickel, platinum and palladium. Homogeneous palladium complexes have emerged as the catalyst of choice for these telomerization reactions, however.

The palladium-catalyzed telomerization of 1,3-butadiene with the generic telogen NuH is given as a prototypical example in Scheme 1. Two products can be obtained, i.e. a linear or branched isomer, depending on the position of nucleophilic attack of the conjugate base of NuH. The linear isomer can be obtained with both *E* and *Z* geometry, with the *E* isomer typically being prevalent. Common side products include 1,3,7-octatriene, the linear dimerization product of 1,3-butadiene without addition of NuH, and to a lesser extent, vinylcyclohexane, the Diels–Alder product of 1,3-butadiene. The challenge in telomerization reactions is generally to limit the oligomerization of the 1,3-diene to dimerization, i.e. to avoid higher oligomers and to produce the linear isomer in high selectivity [1].



Scheme 1 Generalized reaction scheme for the Pd-catalyzed telomerization of 1,3-butadiene with nucleophile NuH

1.1 From Discovery to Commercialization

The telomerization reaction was discovered independently by both Smutny [2] and Takahashi et al. [3] in 1967, while working on the palladium-catalyzed dimerization of 1,3-butadiene. Smutny reported on the reaction between butadiene and phenol, which, in the presence of PdCl_2 as the catalyst and sodium phenoxide as a strong base, gave 96% conversion of phenol to 1-phenoxy-2,7-octadiene. The reaction proved remarkably robust, as it could be run over a broad temperature (0 – 150°C) and pressure range. It was also not sensitive to the addition of poisons and relatively free of by-products. Smutny already noted the importance of the presence of a strong base and that the reaction could also be run neat. In addition to various substituted phenols, other telogens such as carboxylic acids, alcohols and amines all could be successfully converted. The addition of triphenylphosphine to the crude reaction mixture after telomerization, at 0°C , yielded 1,3,7-octatriene after distillation under reduced pressure, already hinting at the fact that product formation is reversible for selected substrates. At around the same time, Takahashi and co-workers used a bis(triphenylphosphine)(maleic anhydride) palladium complex as catalyst in solvents such as acetone, benzene or tetrahydrofuran and first reported the formation of a dimerization product, identified as 1,3,7-octatriene, from butadiene. When done in alcohols or carboxylic acids, a mixture of the telomerization products and 1,3,7-octatriene was obtained. Methanol gave a 90% yield of mainly the linear product, whereas the more sterically hindered alcohol isopropanol mainly led to the production of 1,3,7-octatriene (72% yield based on butadiene) [3]. These first reports on the telomerization reaction thus not only demonstrated the broad scope of this rather versatile reaction, but also already included or pointed at many of the salient features of the process.

Since its discovery in the late 1960s, the telomerization process has matured and been commercialized. The Kuraray company first commercialized an application of the telomerization process in 1991 by producing the plasticizer 1-octanol on a scale of 5,000 ton/year via the dimerization of 1,3-butadiene with the addition of water to

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