Reductive dimerization of dialkyl acetylenedicarboxylate catalyzed by [Rh(binap)(MeOH)$_2$]ClO$_4$ in methanol

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Abstract

Cationic Rh(I) complex [Rh(binap)(MeOH)$_2$]ClO$_4$ catalyzes reductive dimerization of dialkyl acetylenedicarboxylates **1** to give 1,2,3,4-tetrakis(alkoxycarbonyl)-1,3-butadienes **2** in methanol selectively. © 1998 Elsevier Science S.A. All rights reserved.

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It has been well known that oligomerization of acetylene such as cyclotrimerization leading to benzene derivatives or linear dimerization of terminal alkynes leading to ene–yne derivatives is catalyzed by a variety of metal complexes e.g., cobalt, rhodium, zirconium, tantalum [1]. Catalytic hydrodimerization of acetylene leading to 1,3-diene, however, has not so far been reported to the best of our knowledge; only several examples of stoichiometric preparation of conjugated-dienes from acetylenes are known, i.e., formation of 1,3-diene via hydrocupration of terminal acetylenes ([2]a) and the formation of 1,3-diene as a by-product during the reduction of dimethyl acetylenedicarboxylate **1a** with copper(II)/hydrosilanes ([2]b) or sodium hydrogen telluride ([2]c), during the reduction of terminal acetylenes with a cobalt hydride ([2]d), and in the reaction of **1a** with a ruthenium compound ([2]e). Selective catalytic preparation of 'open-chain' conjugated dienes directly from acetylenes are also very rare. Only two examples of synthesis of 1,4-dialkyl conjugated 1,3-dienes catalyzed by palladium complexes using tetramethyltin or tetramethyltin and alkyl halides as alkylating agents have recently been reported [3], though

such direct synthesis of conjugated dienes from alkynes is highly desirable for forming valuable synthetic intermediates [4]. Herein we report on highly selective hydrodimerization of dialkyl acetylenedicarboxylates **1** leading to 'open-chain' 1,3-dienes **2** catalyzed by cationic rhodium(I) diphosphine complexes.

Treatment of diethyl acetylenedicarboxylate **1b** in the presence of a catalytic amount (4 mol%) of [Rh(binap)(MeOH)$_2$]ClO$_4$ [5] (binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) under reflux in methanol gave the hydrodimer, 1,2,3,4-tetrakis(ethoxycarbonyl)-1,3-butadiene **2b**, in 91% yield after 3 h (Eq. 1, Table 1).

The hydrodimer **2b** was comprised of the *Z,Z*- [6,7] and the *E,E*-isomer [7] in a ca. 80:20 ratio accompanied by a small amount of the *E,Z*-isomer and the cyclic trimer, 1,2,3,4,5,6-hexakis(ethoxycarbonyl)benzene **3**. Prolonged heating caused isomerization of the hydrodimer from the *Z,Z*-isomer to the *E,E*-isomer and after heating of 60 h the isomer ratio, *Z,Z*:*E,E* changed to 9:91. This indicates that the initial product should be the *Z,Z*-isomer, which was isomerized to the *E,Z*- and the *E,E*-isomer under the reaction conditions. The mechanism of the isomerization, however, is not clear at present. Ester exchange reactions of the hydrodimer with methanol were also observed and the yield of the tetraethyl esters **2b** decreased to 69%. If the reaction

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Table 1
Catalytic hydrodimerization of dialkyl acetylenedicarboxylate **1** with $[Rh(binap)(MeOH)_2]ClO_4^a$

Entry	Substrate	Reaction temp. (°C)	Reaction time (h)	Yield of **2a** or **2b** (%)[b]	Z,Z:E,E
1	**1b**	20	28	40	72:28
2	**1b**	65	3	91	80:20
3	**1b**	65	60	69[c]	9:91
4	**1a**	20	70	48	73:27
5	**1a**	65	3	81	61:39
6	**1a**	65	20	54	28:72

[a] Conditions: [substrate] = 0.25 M in MeOH; [Rh] = 0.01 M.
[b] Byproducts = cyclic trimer **3**, vinyl ether **4**.
[c] Ester exchanged products of **2b** were also contained as the by-products.

(1)

1

a: R = Me; **b**: R = Et

(Z, Z)-**2**　　　　　(E, E)-**2**
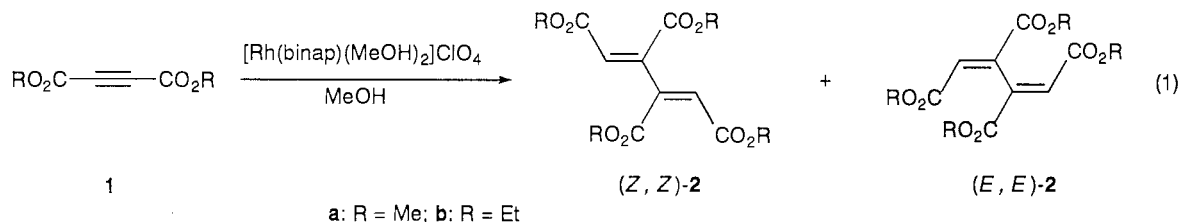
was conducted at 20°C, the starting acetylene was consumed completely after 28 h but the yield of the hydrodirner **2b** was only 40% (Z,Z:E,E = 72:28). The cyclic trimer **3b** and the vinyl ether **4b** [8], obtained by addition of methanol to the acetylene, were obtained as the by-products. Dimethyl acetylenedicarboxylate **1a** similarly reacted under reflux for 3 h to give the corresponding hydrodimer **2a** in 81% yield (Z,Z:E,E:E,Z = 61:39: < 1) accompanied by the cyclic trimer **3a** in 12% yield. Prolonged heating induced second reactions and/or isomerization of the product and the yield of the hydrodimer **2a** decreased again to 54% (Z,Z:E,E = 28:72). The reaction at 20°C after 70 h gave the hydrodimer **2a** in 48% yield (Z,Z:E,E = 73:27). When [Rh(binap)(MeOH)_2]ClO_4 prepared in situ from [Rh(binap)(COD)]ClO_4 (COD = cycloocta-1,5-diene) with dihydrogen in methanol was employed as the catalyst precursor, the reaction of **1b** at 65°C after 20 h gave **2b** in only 40% yield accompanied by 20% of the cyclic trimer **3b** and 35% of the reduction product, diethyl maleate **5b**. This different reactivity between the in situ catalyst and the isolated methanol complex, [Rh(binap)(MeOH)_2]ClO_4, may be due to the presence of the dinuclear complex, [Rh(binap)]_2(ClO_4)_2 [5], in the former system. When an in situ catalyst was used after removing the dinuclear complex by filtration the yield of the hydrodimer **2b** increased to 62%. If [Rh(binap)(cod)]ClO_4 itself was employed as the catalyst precursor without removing the COD ligand by hydrogenolysis, **1b** did not give the hydrodimer **2b** but the vinyl ether **4b** in 34% yield. As the diphosphine ligand, diphos and other peraryldiphosphines, such as 1,2-bis(diphenylphosphino)benzene and 1,1′-bis(diphenylphosphino)ferrocene, were ineffective for the hy-

drodimerization, giving the vinyl ether **4b** and the cyclic trimer **3b** as the main products. Only [Rh(bpbp)(MeOH)_n]^+ (bpbp = 2,2′-bis(diphenylphosphino)1,1′-biphenyl), prepared in situ from [Rh(bpbp)(cod)]ClO_4 and H_2, showed somewhat catalytic activity but **1a** gave the hydrodimer **2a** in only 20% yield, accompanied by a lot of by-products such as **3a**, **4a**, and **5a** in the reaction at 65°C after 20 h.

The source of the hydrogen was found to be the solvent methanol with deuterium-labeling experiments. When the reaction of **1b** by [Rh(binap)(MeOH)_2]ClO_4 was carried out in d_4-methanol the olefinic hydrogen of the hydrodimer **2b** was 100% deuterium, whereas the reaction in CH_3OD only 50% of the olefinic hydrogen was deuterium. Thus, not only the hydroxy hydrogen but also the methyl hydrogen of methanol were used as the hydrogen source. The reaction under hydrogen (60 kg cm^{-2}) at room temperature gave diethyl maleate **5b** as the main product and the hydrodimer **2b** was scarcely obtained. On the basis of these experimental results, a plausible reaction pathway for formation of the Z,Z-isomer (Z,Z-**2**), as well as the formation of **3**, **4**, and **5**, depicted in Scheme 1, is rationally proposed. Consistently, in the reaction mixture, formaldehyde was detected by the chromotropic acid test [9]. Although the present hydrodimerization needs hydrogen transfer from methanol, 2-propanol, which is considered as the best hydrogen source for usual catalytic transfer hydrogenation of carbonyl compounds [10], was not a good solvent and the yield of the hydrodimer **2b** in the reaction in 2-propanol was only 28% accompanied by 56% of the cyclic trimer **3b** and 6% of diethyl maleate **5**. Ethanol was
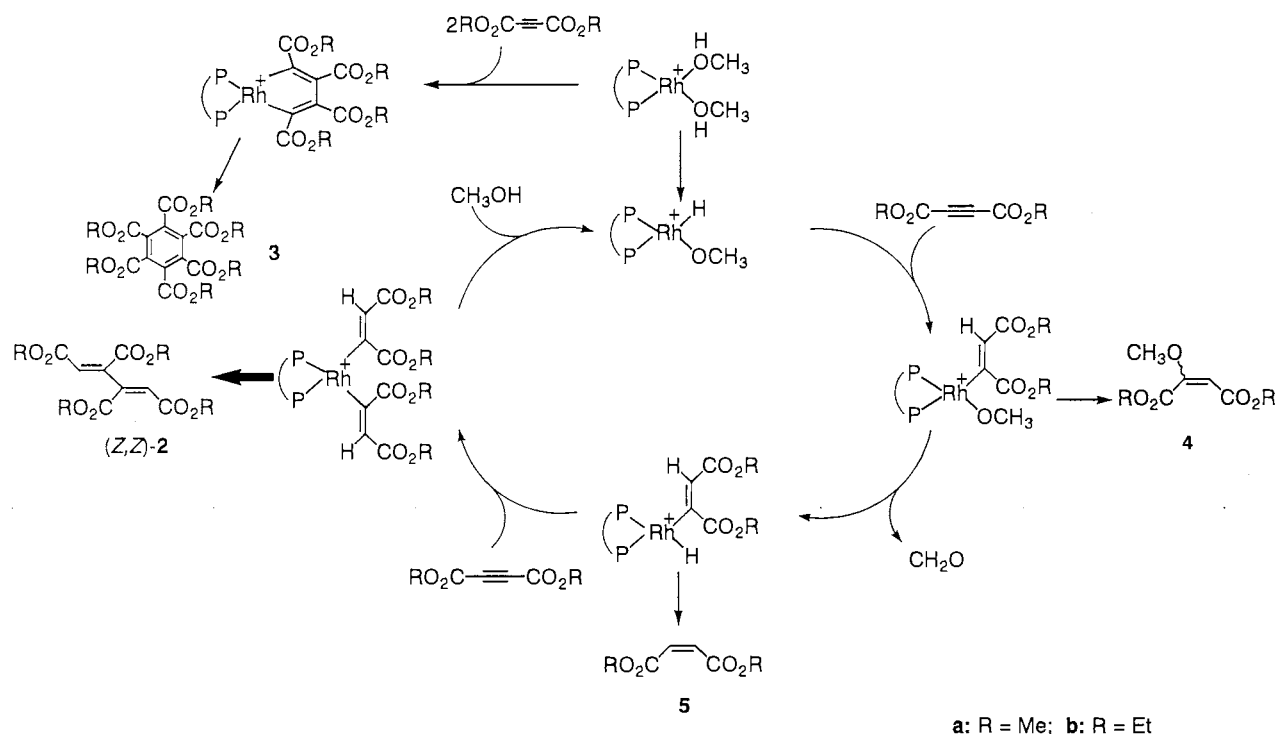
Scheme 1. A plausible reaction pathway for the catalytic reaction of dialkyl acetylenedicarboxylate with [Rh(binap)(MeOH)$_2$]ClO$_4$.

also a good solvent and the hydrodimer **2b** was obtained in 73% yield accompanied by 17% of the cyclic trimcr **3b** and a trace amount of diethyl maleate.

Under similar reaction conditions, ethyl 2-tridecynoate gave only addition products of methanol, ethyl 3-methoxy-2-tridecenoate (48%) and ethyl 3,3-dimethoxytridecanoate (15%) and its hydrolyzed product, ethyl 3-oxotridecanoate (12%). Terminal acetylenes, ethyl propynoate and 1-dodecyne, however, gave a mixture of cyclic trimers, benzene derivatives, in 87 and 71% yields, respectively. Internal acetylenes without carboxylate substituents such as 6-dodecyne and 1,2-diphenylacetylene did not react under similar conditions. Thus, the present hydrodimerization of acetylene leading to conjugated dienes is specific for acetylene dicarboxylates at present. Studies on the detailed mechanism and applicability to other substrates are in progress in our laboratory.

Acknowledgements

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