Synthesis of cross-conjugated trienes by dimerization of allenes with palladium-phenol catalyst

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Cross-conjugated trienes were synthesized by dimerization of monosubstituted allenes in the presence of a catalyst system consisted of $Pd_2(dba)_3$, *p*-nitrophenol, and P(*p*-Tol)$_3$.

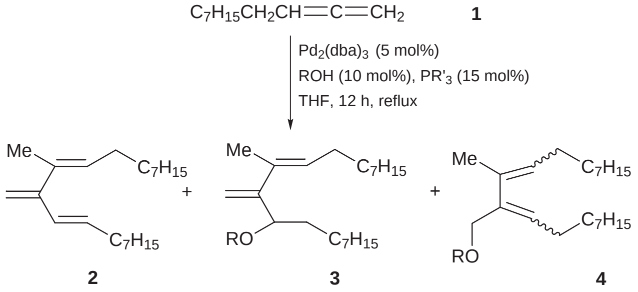
Cross-conjugated trienes have attracted considerable interest in polymer chemistry[1] and theoretical chemistry[2] as well as in synthetic chemistry, and various methods have been developed for the preparation of the parent 3-methylenepenta-1,4-diene and its derivatives.[3] Although catalytic dimerization of substituted allenes can directly provide such trienes, an effective method has as yet not been developed. The dimerization reaction of 3-methylbuta-1,2-diene was reported to give 2,5-dimethyl-3,4-bismethylenehex-1-ene, which was promoted by a stoichiometric amount of a nickel(0) complex.[4] The reaction, however, gave a very low yield of the cross-conjugated triene when other allenes were employed. Although palladium complexes are known to catalyze dimerization of propa-1,2-diene in the presence of water or amine giving hydroxylated or aminated 2,3-dimethylbuta-2,3-diene,[5] the method was not applied to the synthesis of cross-conjugated trienes. Described here is an efficient synthesis of the trienes by catalytic dimerization of monosubstituted allenes, alka-1,2-dienes. A novel combination of $Pd_2(dba)_3$ (dba = dibenzylideneacetone), *p*-nitrophenol, and P(*p*-Tol)$_3$ was employed for the catalyst.

When undeca-1,2-diene **1** was treated with $Pd_2(dba)_3$ (5 mol%), P(*p*-Tol)$_3$ (15 mol%) and *p*-nitrophenol (10 mol%) in refluxing THF for 12 h, (9*E*,12*E*)-10-methyl-11-methyleneicosa-9,12-diene **2** was obtained in quantitative yield (Table 1, entry 5). The structure including the stereochemistry was determined unambiguously by spectroscopic methods. Added phenol played an important role, and no reaction took place in its absence (entry 1). This reaction was effectively promoted by phenol possessing an electron-withdrawing group (*p*-nitrophenol) while the yield of **2** decreased when phenol, alkylphenol, or methoxyphenol was used (entries 2–4). Considerable amounts of adducts **3** or **4** derived from **2** and the phenols were formed in the latter cases. Since AcOH also promoted the reaction (entry 10), phenol appeared to function as the Brønsted acid.[6] The dimerization reaction did not occur with sodium phenoxide or tributyltin phenoxide. Use of P(*p*-Tol)$_3$ was also essential, and the reaction was retarded by the introduction of electron-withdrawing substituents on the aromatic ring (entry 7). Bidentate phosphines gave 1,3-diene without forming the dimeric product (entries 8 and 9).

The dimerization reaction of other methylene-substituted allenes under the above reaction conditions proceeded stereoselectively to give the cross-conjugated (*E*,*E*)-trienes in quantitative yields (Table 2). With this catalyst system, a product–catalyst ratio of 1000:1 could be reached (entry 2). Dimerization of a methyne substituted allene, 1-cyclohexylpropa-1,2-diene, was sluggish, although the stereoselectivity was retained (entry 8).

When **1** was dimerized in the presence of 1.0 equiv. of AcOD (> 99 atom% D) or *p*-$NO_2C_6H_4OD$ (76 atom% D), the dimer **2**-*d* was obtained in 78% yield (79 atom% D) and 93% (56

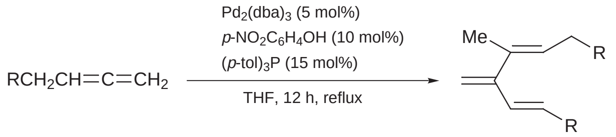
Table 1 Effect of phenol and phosphine on the allene dimerization



Entry	R	R′	Yield (%) 2	Yield (%) recovered 1	Yield (%) 3 and/ or 4
1	none	*p*-Tol	—	95	—
2	*p*-$MeOC_6H_4$	*p*-Tol	60	18	10
3	*p*-Tol	*p*-Tol	54	7	9
4	Ph	*p*-Tol	91	—	4
5	*p*-$NO_2C_6H_4$	*p*-Tol	96	—	—
6	*p*-$NO_2C_6H_4$	Ph	89	—	—
7	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	57	20	—
8	*p*-$NO_2C_6H_4$	dppe[a]	—	42	—[b]
9	*p*-$NO_2C_6H_4$	dppf[c]	—	—	—[d]
10	Ac	*p*-Tol	74	—	—

[a] 1,2-Diphenylphosphinoethane. [b] Undeca-1,3-diene was obtaiend in 36% yield. [c] 1,1′-Bis(diphenylphosphino)ferrocene. [d] Undeca-1,3-diene was obtained in 71% yield.

Table 2 Synthesis of cross-conjugated trienes by the allene dimerization reaction



Entry	Allene	Yield (%)
1	$C_7H_{15}CH_2CH_2{=}C{=}CH_2$	96
2	$C_7H_{15}CH_2CH{=}C{=}CH_2$	99[a]
3	$C_5H_{11}CH_2CH{=}C{=}CH_2$	96
4	$Bu^tMe_2SiOCH_2CH_2CH{=}C{=}CH_2$	96
5	$Bu^tMe_2SiO(CH_2)_2CH_2CH{=}C{=}CH_2$	89
6	$PhCH_2CH{=}C{=}CH_2$	93
7	$PhCH_2CH_2CH{=}C{=}CH_2$	99
8	*c*-$C_6H_{11}CH{=}C{=}CH_2$	36[b]

[a] The reaction was carried out using 5 mmol of **1** in the presence of 0.1 mol% of $Pd_2(dba)_3$, 0.3 mol% of P(*p*-Tol)$_3$ and 0.2 mol% of *p*-nitrophenol. [b] Starting material was recoverd in 32% yield.

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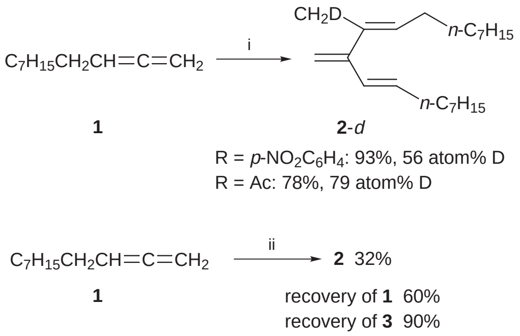
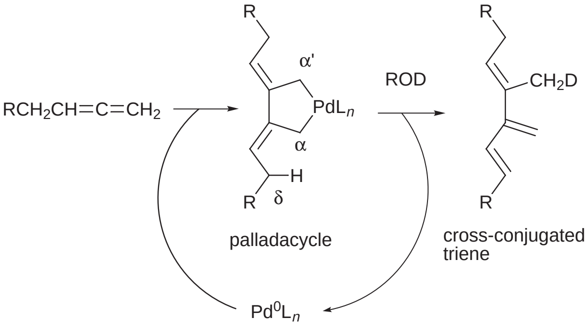


Scheme 1 *Reagents and conditions*: i, $Pd_2(dba)_3$ (5 mol%), P(*p*-Tol)$_3$ (15 mol%), ROD (100 mol%), THF, reflux, 12 h; ii, $Pd_2(dba)_3$ (5 mol%), P(*p*-Tol)$_3$ (15 mol%), **3** (R = *p*-Tol) (10 mol%), THF, reflux, 12 h.

atom% D) yield, respectively (Scheme 1). A ^{2}H NMR experiment revealed deuteration at the methyl group. A considerable part of the proton was thus introduced from the external proton source. In order to know the role of the adducts **3** and **4** in the reaction, the dimerization of **1** was conducted in the presence of a catalytic amount of **3** (R = *p*-Tol) instead of *p*-nitrophenol. After reacting for 12 h, only 32% yield of the dimer **2** was obtained with **1** recovered in 60% yield. Approximately 90% of the adduct **3** (R = *p*-Tol) was also recovered unchanged. The result, compared to that of Table 1, entry 3, indicated that the formation of **3** and **4** was not the major process of the present catalytic reaction.

Although the dimerization reactions of propa-1,2-diene and 3-methylbuta-1,2-diene was studied to some extent,[4,5] the mechanism still remained unclear. Based on our experiments and the results of the $(R_3P)_3Ni$-promoted stoichiometric dimerization reaction of 3-methylbuta-1,2-diene, the following working hypothesis was presented (Scheme 2). Since the nickel reaction took place *via* a nickelacycle,[4] it may be likely that the present palladium-catalyzed dimerization involved a palladacycle.[7] The reductive elimination with concomitant proton transfer from the δ-carbon atom to the α'-carbon atom gave the cross-conjugated triene. Our deuteration experiments showed that the δ-proton in the palladacycle was not transferred intramolecularly. The process appeared to be catalyzed by phenol.



Scheme 2

Polymerization of the cross-conjugated trienes obtained in the present study was also examined. Triene **2** was treated with $SnCl_4$ and Bu^{t}Cl in CH_2Cl_2 at −50 °C for 1 min.[8] After aqueous workup and purification by gel permeation chromatography, soluble polymer was obtained in 30% yield (M_n = 1.9 × 10^4, M_w/M_n = 1.93). Use of protic acid (H_2SO_4, $HClO_4$, TfOH) gave insoluble materials. The cationic conditions turned out to be suitable for the polymerization of **2**, and radical conditions (AIBN, 80 °C), anion treatment (Bu^{n}Li or Bu^{t}Li, THF, −78 °C) or thermal treatment (80 °C, 24 h, under argon or oxygen) gave low molecular weight oligomers.

The dimerization reaction of **1** is representative. Under an argon atmosphere, a mixture of $Pd_2(dba)_3$ (45.7 mg, 5 mol%), P(*p*-Tol)$_3$ (45.6 mg, 15 mol%), **1** (152 mg, 1.0 mmol) and *p*-nitrophenol (13.9 mg, 10 mol%) in THF (5 ml) was heated at reflux for 12 h. THF was then removed under reduce pressure, and the residue was purified by flash chromatography (hexane) over silica gel giving **2** (145.9 mg, 96%).

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Notes and references

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