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Hexacarbonylmolybdenum(0)-Catalyzed Reductive Coupling of Allylic Acetates

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Synopsis. The reaction of allylic acetates with zinc in the presence of a catalytic amount of hexacarbonylmolybdenum(0) led to reductive coupling for the formation of a 1,5-diene framework. Reductive coupling of nerolidyl acetate provided squalene and its isomers in high yield.

Allylic halides have been generally employed in reductive coupling for the formation of 1,5-diene frameworks.[1] Recently, instead of the unstable allylic halides, allylic acetates which are easier to prepare and store than the halides have been applied in the palladium-catalyzed reductive coupling via π-allylpalladium complex with zinc.[2] On the other hand, hexacarbonylmolybdenum(0), which is relatively inexpensive and is stable against oxygen and moisture, reacts with allylic acetates to form π-allylmolybdenum complexes.[3] Hexacarbonylmolybdenum(0) is likely to become a convenient catalyst for the reductive coupling of allylic acetates with zinc.

The molybdenum-catalyzed reductive coupling of cinnamyl acetate was carried out under various reaction conditions, as summarized in Table 1. The coupling reaction did not occur in refluxing toluene, which had been effective in hexacarbonylmolybdenum(0)-catalyzed reactions of the allylic acetates with carbon nucleophiles, and did not also occur in refluxing dioxane or in DMF at 110 °C (Entries 1—3). Next, the effect of ligands was investigated. The addition of 10 mol% of 2,2′-bipyridyl (bpy) accelerated the reaction in refluxing dioxane and THF (Entries 4 and 5). Ligands such as *N,N,N′,N′*-tetramethyl-1,2-ethanediamine, *N,N,N′,N′*-tetramethyl-1,3-propanediamine, and triphenylphosphine were not effective under the same conditions. Accordingly, the reductive coupling of various allylic acetates was carried out in refluxing dioxane containing 10 mol% of bpy. The reaction of 3-acetoxy-1-octene produced 6,10-hexadecadiene (48%)[4] and 9-vinyl-6-tetradecene (52%)[4] in 54% yield. The reaction of (*E*)-3-acetoxy-1-phenyl-1-butene also provided (1*E*,5*E*)-3,4-dimethyl-1,6-diphenyl-1,5-hexadiene (42%), 4,5-diphenyl-2,6-octadiene (8%),[4] and 1,4-diphenyl-3-methyl-1,5-heptadiene (50%)[4] in 37% yield. However, 3-acetoxy-1-cyclohexene did not cause the reductive coupling.

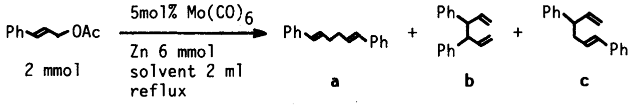
Reactivity and regio- and stereoselectivity were investigated in the reductive coupling of terpenoid allylic acetates such as linalyl, neryl, geranyl, nerolidyl, and farnesyl acetate. The results are summarized in Table 2. Zn–Cu couple as a reducing agent, compared with zinc powder, accelerated the reaction of linalyl acetate (Entries 1 and 2). The difference in the reactivity between linalyl acetate and neryl and geranyl acetate may be due to the difference in the rate of the formation of π-allylmolybdenum complexes (Entries 2—4).[3] In every case (Entries 1—4), the ratios of regioisomers (**I**/**II**) are similar, about 25/75. Being distinct from palladium-catalyzed reductive coupling,[2] stereoselectivities did not depend on the substrates (**a**:**b**=ca. 30:70, **c**:**d**:**e**=ca. 10:50:40). It is presumed from the results that the reductive couplings proceed after syn/anti isomerization of the π-allylmolybdenum complexes occurs to reach the equilibrium,[3] in contrast with the π-allylpalladium complexes which do not cause the syn/anti isomerization.[5] Using this method, nerolidyl acetate, which was more reactive than farnesyl acetate, was reduced to give squalene and its isomers as coupling products (Entries 5 and 6).

As mentioned above, hexacarbonylmolybdenum(0) proved to be a good catalyst for the reductive coupling of allylic acetates.

Experimental

General Procedure of Hexacarbonylmolybdenum(0)-Catalyzed Reductive Coupling of Allylic Acetates. To a solution of allylic acetate (2 mmol), zinc powder (0.39 g, 6

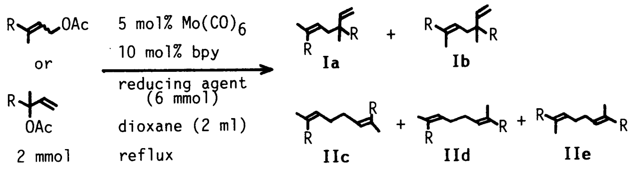
Table 1. Reductive Coupling of Cinnamyl Acetate

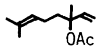
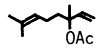
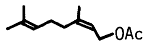
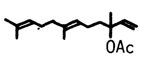


Entry	Solvent	bpy/mol%	Reaction time/h	Yield$^{a)}$/%	Ratio$^{b)}$		
					a	**b**	**c**
1	toluene	—	50	0	—		
2	DMF$^{c)}$	—	68	9	34	0	66
3	dioxane	—	52	8	39	0	61
4	dioxane	10	10	77	47	4	49
5	THF	10	20	79	47	5	48
6	benzene	10	70	13	49	7	44

a) Isolated yields. b) The isomer ratios were determined by GLPC [5% OV-17/Chromosorb W (AW-DMCS), 60—80 mesh, 2 m, 230 °C] and 200 MHz ^{1}H NMR (Jeolco FX-200). c) Reaction temp 100 °C.

Table 2. Reductive Coupling of Terpenoid Allylic Acetates



Entry	Allylic acetate	Reducing agent	Reaction time/h	Yield[a]/%	Ratio[b] I : II (a : b) (c : d : e)
1		Zn	27	55	27 : 73 (30:70) (11:49:40)
2		Zn-Cu	8	85	23 : 77 (29:71) (10:48:42)
3		Zn-Cu	66	57	27 : 73 (31:69) (10:50:40)
4		Zn-Cu	96	15	27 : 73 (32:68) (12:50:38)
5		Zn	72	75	25 : 75 (31:69) (14:47:39)
6		Zn-Cu	115	20	20 : 80 (30:70) (10:48:42)

a) Isolated yields. b) The isomer ratios were determined by GLPC [5% OV-17/Chromosorb W (AW-DMCS), 60—80 mesh, 2 m, He, 160 °C (Entries 1—4), 200 °C (Entries 5 and 6).

mmol), and bpy (31 mg, 0.2 mmol) in dioxane (2 ml) was added hexacarbonylmolybdenum(0) (26 mg, 0.1 mmol). The mixture was refluxed for 8—115 h under a nitrogen atmosphere. The reaction mixture was diluted with ether (50 ml), washed with 10% HCl soln (20 ml) followed by water (2X20 ml), and dried over $MgSO_4$. Evaporation of ether and column chromatography on silica gel (Wakogel C-200) using hexane or hexane/EtOAc as the eluent gave coupling products. The structures and isomer ratios were determined by comparison with GLPC and ^{1}H NMR results of the samples prepared by the alternative method.[2]

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2) S. Sasaoka, T. Yamamoto, H. Kinoshita, K. Inomata, and H. Kotake, *Chem. Lett.*, **1985**, 315 and references cited therein.

3) B. M. Trost and M. Lautens, *J. Am. Chem. Soc.*, **104**, 5543 (1982); *idem, ibid.*, **105**, 3343 (1983).

4) The stereochemistry was not confirmed by GLPC and ^{1}H NMR.

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