Tetrahedron Letters,Vol.27,No.14,pp 1615-1616,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

ALLYLIC GEMINAL DIACETATES AS A a^1,a^3 SYNTHON. A CONVENIENT SYNTHESIS OF BICYCLO[3.3.1]NONAN-9-ONE DERIVATIVES

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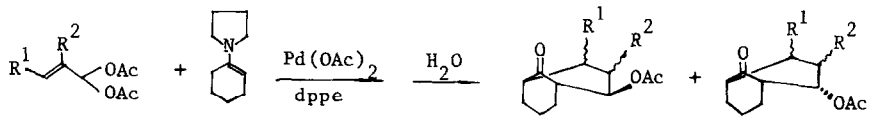
Abstract: 2-Acetoxy bicyclo[3.3.1]nonan-9-one derivatives could be systhesized from the reaction of allylic 1,1-diol diacetates(1) with pyrrolidine enamine of cyclohexanone under the catalysis of palladium complex in one step.

Palladium-catalyzed reaction of carbanions with diacetates of allylic 1,1-diols(1) has been studied by Lu and Trost under different conditions[1,2]. The reaction of enamines with π-allylpalladium complex has been studied by Murahashi[3]. We wish to report here our recent results of the reactions of enamine with 1. We found that the reaction of allylic 1,1-diol diacetates (1) with pyrrolidine enamine of cyclohexanone under the catalysis of palladium yields 2-acetoxy bicyclo[3.3.1]nonan-9-one derivatives, which has the peculiar carbon skeleton of natural products[4-6].

The following procedure is typical: After stirring a mixture of 1,1-diacetoxy 2-propene(1a, 316mg, 2 mmol), $Pd(OAc)_2$ (22mg,0.1 mmol), dppe(40mg, 0.1 mmol) and THF(10 ml)for 10min., N-(1-cyclohexenyl)pyrrolidine (2,300mg, 2 mmol) was added with a syringe under argon atmosphere. The mixture was heated at reflux for 16h. After removal of THF in vacuo, the residue was hydrolyzed by treatment with water (10 ml) at 100°C (2 h.) and extracted with ether. The ether extract was washed with aqueous $NaHCO_3$, dried and concentrated. The residue was distilled by short path distillation to give a colorless liquid, b.p 80-100°C (oil bath)/ 0.3mmHg., 150mg, yield 38%. Flash chromatography was used for further purification (petroleum ether/ ethyl acetate=5/1).



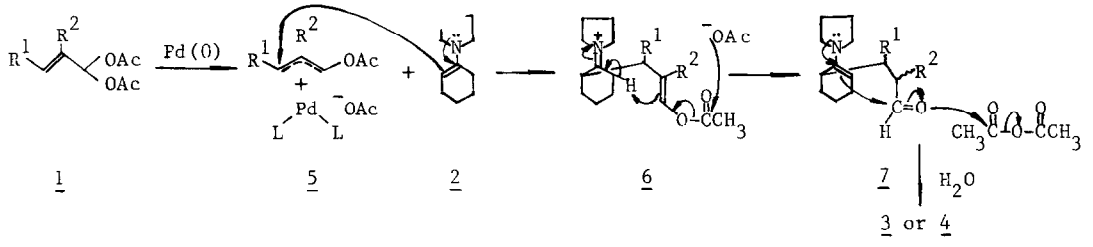
1 2 3 4

Synthesis of bicyclo[3.3.1]nonan-9-one derivatives

Compound	R^1	R^2	Yield (%)	Products 3	4
1a	H	H	38	100	0
1b	CH_3	H	30	100	0
1c	H	CH_3	43	83	17

The probable reaction mechanism is shown in scheme 1. The enamine reacts first with the π-allylpalladium complex 5 to give 6 and acetate anion, which attacks the carbon atom of the carbonyl group of the remaining acetoxy group to form acetic anhydride and 7. Then,the newly formed enamine(7) attacks aldehyde group intramolecularly and the latter reacts with acetic anhydride followed by hydrosis to yield 3 and 4.

SCHEME 1



1 5 2 6 7

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7. 3a: b.p.80-100°C(oil bath)/0.3 Torr; IR(neat): 1740(vs),1720(s); MS: 196(M^+), 136, 108,55,43; ^{1}H NMR($CDCl_3$,60MHz): 5.25(m,1H),2.45(m,2H),2.3-1.35(m,10H), 2.0(s,3H); ^{13}C NMR($CDCl_3$, 90MHz): 217.3, 169.7, 78.3, 51.2, 45.9, 34.8, 31.0, 28.8, 26.3,21.1, 19.6. (Literature data: see reference 8). 3b: b.p.80-120°C (oil bath)/0.3 Torr; IR(neat): 1740(vs),1720(s); MS: 210(M^+), 150,128, 107, 55,43; ^{1}H NMR($CDCl_3$, 60MHz) 5.2(m,1H), 2.45(m,2H), 2.4-1.4(m, 9H),2.0(s,3H), 1.06(d,3H,J=6Hz); ^{13}C NMR($CDCl_3$,90MHz): 217.6, 169.9,77.4, 51.7, 50.3, 34.5, 30.5, 28.5, 26.3,21.1, 19.6, 18.4. Elem. anal. calcd. for $C_{12}H_{18}O_3$: C,68.54; H, 8.62;found: C,68.40; H,8.76. 3c: m.p.54-55°C (from subimation); IR:(neat) 1740(vs), 1720(s); MS: 311(M+1),168, 151, 122, 55, 43; ^{1}H NMR($CDCl_3$,60MHz): 5.2(t,1H,J=3Hz), 2.45(m, 2H), 2.05(s, 3H), 2.4-1.4(m, 9H), 0.95(d,3H,J=7Hz); ^{13}C NMR($CDCl_3$,90MHz): 217.9, 170.0, 80.9, 50.9, 45.9, 37.6, 34.6, 30.8,30.1, 20.8, 20.0, 17.0; Elem. anal. calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.62; found: C, 68.52; H,8.70. 4c: b.p. 84-85°C/0.2 Torr; IR: (neat): 1740(vs), 1720 (s); MS: 211(M^++1), 151, 122, 55, 43; ^{1}H NMR (CCl_4,60MHz): 4.65(m,1H), 2.45(m,2H), 2.4-1.35 (m,9H), 2.05(s, 3H), 0.98(broad,3H); Calcd exact mass for $C_{12}H_{18}O_3$: 210.126; found: 210.125.

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(Received in Japan 18 January 1986)