Double Acylation of Alkenes with Acylchromates Promoted by Cationic Pd(II) Complex

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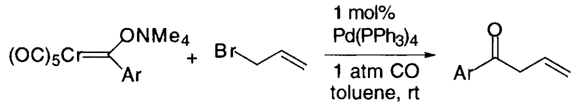
Double acylation of alkenes such as norbornene and vinylsilane proceeds by the use of acylchromate complexes and a cationic Pd(II) complex. When two different acylchromates are added successively to a mixture of alkene and the Pd complex, unsymmetrical diketones are obtained almost selectively.

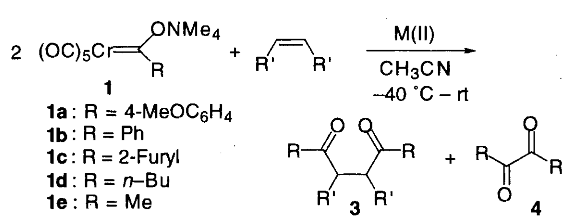
Palladium catalyzed carbonylation reactions have found a wide application in organic synthesis, where acylpalladium complexes play an important role as key intermediates.[1] Generally, acylpalladium species are generated by two methods; (i) oxidative addition of acyl halides to Pd(0) complexes (ii) insertion of carbon monoxide to alkylpalladium complexes. As compared with these methods, metal exchange between acylmetals and Pd(II) compounds has not found a wide utility due to the limitation of acylmetals suitable for transmetallation. Though acyl stannanes,[2] iron,[3] nickel,[3] and zirconium[4] compounds have been employed as acyl sources, these acylmetals have some drawbacks such as difficulty of their synthesis, instability in the air, toxicity, or necessity of high temperature in the transmetallation step.

Tetraalkylammonium acylchromates are relatively stable and easy to be synthesized. Recently, we reported that Pd(0)-catalyzed acylation reactions of allylic halides by using acylchromates **1** as donors of acyl groups (eq. 1).[5]



(1)

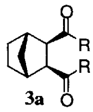
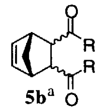
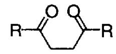
Because the metal exchange between acylchromates and η^3–allylpalladium(II) species seems to proceed at low temperature in the above reaction, we expected that double acylation of alkenes would proceed with acylchromates and Pd(II) as depicted in eq. 2.[6]



(2)

Acylation of norbornene was firstly examined with Pd(II) and 2 molar amounts of tetramethylammonium *p*–methoxybenzoylchromate **1a**. The use of $Pd(OAc)_2$ and $PdCl_2(CH_3CN)_2$ were found to give the double acylation product **3a** in 35% and 62%, respectively, however, α–diketone **4a**, a dimer of the chromate **1a**, was detected as a side product (Table 1, entries 1 and 2). As it is known that cationic acylpalladium(II) species exhibit higher reactivity in the addition reaction to alkenes than neutral acylpalladiums, the acylation was examined with $Pd(CH_3CN)_4(BF_4)_2$ (**2**).[7] In fact, the double acylation product **3a** was obtained in 84% yield without the formation of **4a** (entry 3). Thus palladium complexes particularly the cationic complex promoted the double acylation, whereas **3a** was not obtained in the reaction with Pt and Ni compounds (entries 4 and 5).

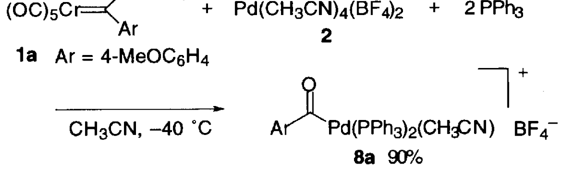
Table 1. Symmetric double acylation of alkenes

Entry	[Cr]1	Alkene	M(II)	Product	Yield / %		
1	**1a**		$Pd(OAc)_2$	 **3a**	35	**4a**	30
2	**1a**		$PdCl_2(CH_3CN)_2$	**3a**	62	**4a**	<14
3	**1a**		$Pd(CH_3CN)_4(BF_4)_2$ (**2**)	**3a**	84	**4a**	–
4	**1a**		$NiCl_2(PPh_3)_2$	**3a**	–	**4a**	–
5	**1a**		$PtCl_2(cod)$	**3a**	trace	**4a**	–
6	**1b**		**2**	**3b**	83	**4b**	–
7	**1c**		**2**	**3c**	77	**4c**	–
8	**1d**		**2**	**3d**	87	**4d**	–
9	**1b**		**2**	 **5b**[a]	74	**4b**	–
10	**1b**	SiMe2Ph	**2**	 **6b**	66	**4b**	13

[a] *cis-exo* : *cis-endo* = 2:1

Double acylation of norbornene with aroyl chromates **1a**–**c** and the cationic palladium complex **2** proceeds smoothly to afford the *cis*–*exo* diketones **3a**–**c** stereoselectively in good yield (entries 3, 6 and 7).[8,9] Alkanoylchromate **1d** is also utilizable for this reaction (entry 8). When norbornadiene is employed instead of norbornene, two *cis* diacylated products **5b**, *cis-exo* and *cis-endo* diacylnorbornenes are obtained in a 2:1 ratio (entry 9).[9] In addition to norbornene derivatives, dimethylphenylvinylsilane can be transformed to diphenyl-1,4-butanedione **6b** (entry 10).

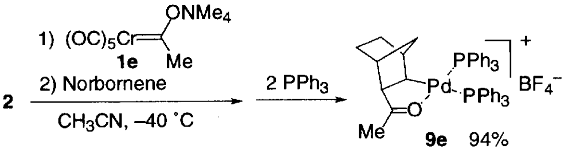
The acyl transfer from acylchromate complex **1** to $Pd(CH_3CN)_4(BF_4)_2$ (**2**) was confirmed by isolating an acylpalladium intermediate. When $Pd(CH_3CN)_4(BF_4)_2$ (**2**) was treated with **1a** and triphenylphosphine in a 1:1:2 molar ratio, acylpalladium complex **8a** was isolated in 90% yield (eq. 3). The chemical shift of ^{13}C-NMR (δ_{CO}: 218.5 ppm) and IR spec-



(3)

tra (ν_{CO}: 1666, 1643 cm^{-1}) of **8a** support the structure of acylpalladium complex by the comparison with those of analogous acylpalladium complexes in the literatures.[7a]

The isolation of a norbornene inserted intermediate was also investigated by using acylchromate **1e**. After the reaction of **1e**, **2** and norbornene, the resulting intermediate was trapped with triphenylphosphine to give the known complex, 3-acetylnorborn-2-ylpalladium **9e** (eq. 4).[7a]

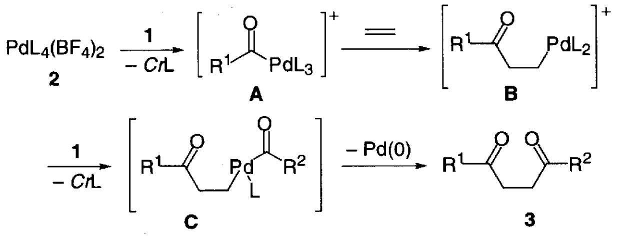


(4)

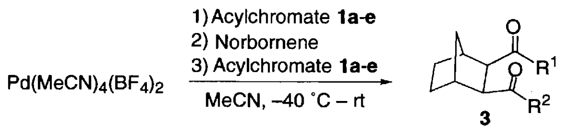
These results suggested the following reaction mechanism. The metal exchange between **1** and **2** affords acylpalladium(II) species **A**, which is converted to norbornyl palladium(II) intermediate **B**. Then the acylation of the palladium with the second acylchromate **1** forms acyl alkyl palladium complex **C**, and the successive reductive elimination affords the double acylation product **3** (Scheme 1).

Scheme 1. Proposed mechanism of double acylation reaction.

L = MeCN, *Cr* = (OC)$_5$Cr



This mechanistic consideration prompted us to investigate the unsymmetrical double acylation by the use of different acylchromates ($R_1 \neq R_2$ in Scheme 1). In fact, the successive addition of two different acylchromates to a mixture of **2** and norbornene realized the unsymmetrical three-component coupling as shown in Table 2. Various unsymmetrical *cis-exo* diacylnorbornanes are prepared in high yields. Though symmetrical diketones originated from the latter acylchromates were detected, the unsymmetrical diketones **3** were prepared almost selectively.



(5)

Table 2. Unsynmetrical double acylation of norbornene

Entry	First Acylchromate		Second Acylchromate		Product		Yield	
	R^1	**1**	R^2	**1**		**3**	/ %	
1	Ph	**1b**	4-MeOC$_6$H$_4$	**1a**	**3ab**	85	**3a**	7
2	4-MeOC$_6$H$_4$	**1a**	Ph	**1b**	**3ab**	80	**3b**	8
3	Ph	**1b**	*n*–Bu	**1d**	**3bd**	68	**3d**	8
4	*n*–Bu	**1d**	Ph	**1b**	**3bd**	78	**3b**	6
5	Ph	**1b**	Me	**1e**	**3be**	65	**3e**	<20
6	Me	**1e**	Ph	**1b**	**3be**	75	**3b**	7

As described above, a double acylation reaction of alkenes is achieved by the use of acylchromates as acyl donors and the cationic palladium(II) complex.

References and Notes

1 a) J. Tsuji, *Acc. Chem. Res.*, **2**, 144 (1969). b) J. K. Stille, L. F. Fries, R. W. Fries, P. K. Wong, D. E. James, and K. S. Y. Lau, *Adv. Chem. Ser.*, **57**, 1799 (1974). c) J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer Verlag, Heiderberg (1980). d) A. Yamamoto, T. Yamamoto, and F. Ozawa, *Pure & Appl. Chem.*, **57**, 1799 (1985). e) D. Milstein, *Acc. Chem. Res.*, **21**, 428 (1988). f) E. Drent, *Pure Appl. Chem.*, **62**, 661 (1990). g) A. Sen, T. -W. Lai, *J. Am. Chem. Soc.*, **104**, 3520 (1982). h) E. Drent, J. A. M. van Broekhoven, and M. J. Doyle, *J. Organomet. Chem.*, **417**, 235 (1991). i) K. Nozaki, N. Sato, Y. Tonomura, M. Yasutomi, H. Takaya, T. Hiyama, T. Matsubara, and N. Koga, *J. Am. Chem. Soc.*, **119**, 12779 (1997). j) F. J. Parlevliet, M. A. Zuideveld, C. Kiener, H. Kooijman, A. L. Spek, P. C. J. Kamer, and P. W. N. M. van Leeuwen, *Organometallics*, **18**, 3394 (1999), and references cited therein.

2 J.-B. Verlhac, E. Chanson, B. Jousseaume, and J.-P. Quintard, *Tetrahedron Lett.*, **49**, 6075 (1985).

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4 Y. Hanzawa, N. Tabuchi, and T. Taguchi, *Tetrahedron Lett.*, **39**, 6249 (1998). Y. Hanzawa, N. Tabuchi, K. Saito, S. Noguchi, and T. Taguchi, *Angew. Chem., Int. Ed. Engl.*, **38**, 2395 (1999).

5 H. Sakurai, K. Tanabe, and K. Narasaka, *Chem. Lett.*, **1999**, 309.

6 Recently, a Pd-catalyzed double benzoylation of norbornadiene was reported, which was carried out by using diphenyliodonium tetrafluoroborate and phenylboronic acid at atmospheric pressure of carbon monoxide, see: S.-K. Kang, J.-S. Kim, S.-C. Choi, and K.-H. Lim, *Synthesis*, **1998**, 1249.

7 Mechanistic studies of the insertion of alkenes into cationic acylpalladium complexes, see: a) J. S. Brumbaugh, R. R. Whittle, M. Parvez, and A. Sen, *Organometallics*, **9**, 1735 (1990). b) F. Ozawa, T. Hayashi, H. Koide, and A. Yamamoto, *J. Chem. Soc., Chem. Commun.*, **1991**, 1469, and references cited therein.

8 The representative procedure is as follows. To an acetonitrile solution of 47.3 mg (0.106 mmol) of Pd(MeCN)$_4$(BF)$_4$, 39.5 mg (0.106 mmol) of tetramethylammonium salt of benzoylchromate complex **1b** was added dropwise at –40 °C for over 30 minutes. Then 49.7 mg (0.530 mmol) of norbornene was added, followed by the successive addition of 39.5 mg (0.106 mmol) of **1b**. The reaction mixture was allowed to room temperature, then stirred for 12 h.

9 The stereochemistry of the 2,3-bis(acyl)norbornanes and norbornenes was determined by comparison with the chemical shift of ^{1}H-NMR and ^{13}C-NMR in the literatures, see: F. Freeman, M. Y. Lee, H. Lu, and X. Wang, *J. Org. Chem.*, **59**, 3695 (1994). S. Arakawa, *J. Org. Chem.*, **42**, 3800 (1977) and Ref. 6.