

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

Motoki Yamane, Yuichiro Ishibashi, Hidehiro Sakurai, and Koichi Narasaka*

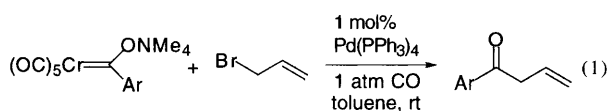
Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033

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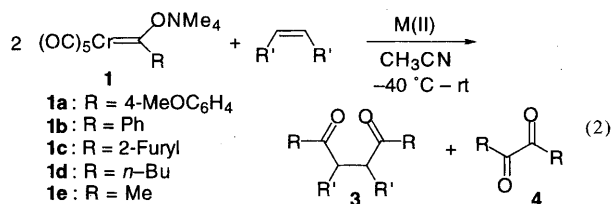
Double acylation of alkenes such as norbornene and vinylsilane proceeds by the use of acylchromate complexes and a cationic Pd(II) complex. When two different acylchromates are added successively to a mixture of alkene and the Pd complex, unsymmetrical diketones are obtained almost selectively.

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 transmetalation. Though acyl stannanes,² iron,³ nickel,³ and zirconium⁴ 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 transmetalation 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

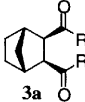
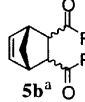


Because the metal exchange between acylchromates and η^3 -allylpalladium(II) species seems to proceed at low temperature in the above reaction, we expected that double acylation of alkenes would proceed with acylchromates and Pd(II) as depicted in eq. 2.⁶



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 PdCl₂(CH₃CN)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

Table 1. Symmetric double acylation of alkenes

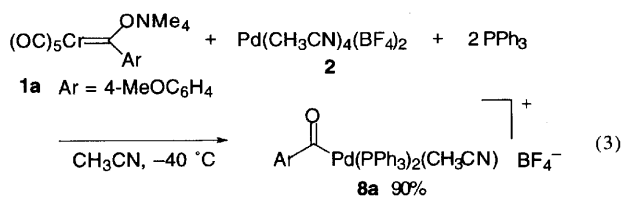
Entry	[Cr] 1	Alkene	M(II)	Product	Yield / %
1	1a		Pd(OAc) ₂		35 4a 30
2	1a		PdCl ₂ (CH ₃ CN) ₂	3a	62 4a <14
3	1a		Pd(CH ₃ CN) ₄ (BF ₄) ₂ (2)	3a	84 4a -
4	1a		NiCl ₂ (PPh ₃) ₂	3a	- 4a -
5	1a		PtCl ₂ (cod)	3a	trace 4a -
6	1b		2	3b	83 4b -
7	1c		2	3c	77 4c -
8	1d		2	3d	87 4d -
9	1b		2		74 4b -
10	1b		2		66 4b 13

^a *cis-exo* : *cis-endo* = 2:1

Pd(CH₃CN)₄(BF₄)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).

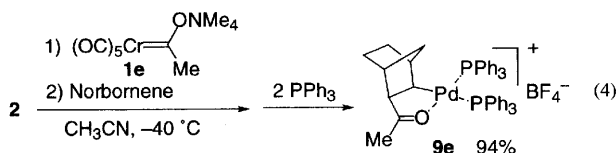
Double acylation of norbornene with aryl chromates **1a-c** and the cationic palladium complex **2** proceeds smoothly to afford the *cis-exo* diketones **3a-c** stereoselectively in good yield (entries 3, 6 and 7).^{8,9} Alkanoylchromate **1d** is also utilizable for this reaction (entry 8). When norbornadiene 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(CH₃CN)₄(BF₄)₂ (**2**) was confirmed by isolating an acylpalladium intermediate. When Pd(CH₃CN)₄(BF₄)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 ¹³C-NMR (δ_{CO} : 218.5 ppm) and IR spec-



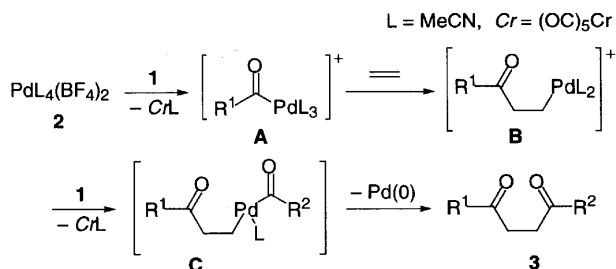
tra (ν_{CO} : 1666, 1643 cm^{-1}) of **8a** support the structure of acylpalladium complex by the comparison with those of analogous acylpalladium complexes in the literatures.^{7a}

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}



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.



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.

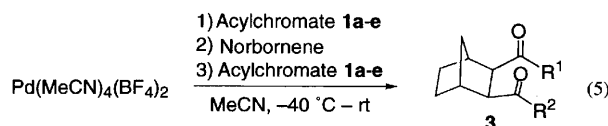


Table 2. Unsymmetrical double acylation of norbornene

Entry	First Acylchromate R^1	Second Acylchromate R^2	Product 3	Yield / %
1	Ph	4-MeOC ₆ H ₄	3ab	85
2	4-MeOC ₆ H ₄	Ph	3ab	80
3	Ph	<i>n</i> -Bu	3bd	68
4	<i>n</i> -Bu	Ph	3bd	78
5	Ph	Me	3be	65
6	Me	Ph	3be	75

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

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- Recently, a Pd-catalyzed double benzylation 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.
- 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.
- The representative procedure is as follows. To an acetonitrile solution of 47.3 mg (0.106 mmol) of $\text{Pd}(\text{MeCN})_4(\text{BF}_4)_4$, 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.
- The stereochemistry of the 2,3-bis(acyl)norbornanes and norbornenes was determined by comparison with the chemical shift of ^1H -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.

