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PALLADIUM-CATALYZED ACYLATION OF ACTIVATED ALKENES WITH BRIDGEHEAD ACID CHLORIDES

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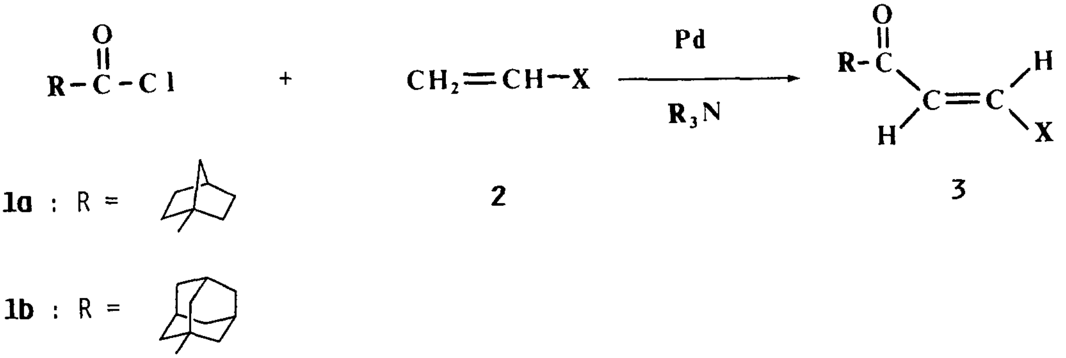
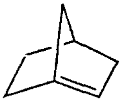
Summary: *Bridgehead acid chlorides* **1a** *and* **1b** *react with activated alkenes* **2** *in the presence of a catalytic amount of palladium and 1 equiv of a tertiary amine. The reaction proceeds regio- and stereoselectively at the terminal carbon atoms to yield acylated alkenes* **3** *with E-configuration.*

Acylpalladium complexes are important organometallic species in the palladium-catalyzed carbonylation of alkenes, alkynes, and organic halides.[1] Palladium-catalyzed decarbonylation[2] of acid chlorides and cross-coupling reactions[3] of organometallics with acid chlorides are also believed to involve acylpalladium complexes. There have appeared several intramolecular cyclizations of acylpalladium complexes bearing an olefinic group in the molecules.[4-7] However, little is known about intermolecular acylpalladation of alkenes.[8] The acylated styrene derivative has been isolated as a minor product from metallic palladium-catalyzed decarbonylation of phenylpropionyl chloride.[2a] Insertion of ethylene into palladium-acyl bond has been observed in the palladium-catalyzed copolymerization of carbon monoxide with ethylene.[9] In this letter, we wish to report a novel palladium-catalyzed intermolecular acylation of activated alkenes 2 with bridgehead acid chlorides 1.



During the course of our studies on the syntheses and reactions of tricyclic alkenes,[10] we have found[11] that decarbonylation of some tricyclic bridgehead acid chlorides proceeds under mild conditions with palladium catalyst in the presence of tri-*n*-butylamine to give exclusively stable disubstituted olefins with intermediacy of the strained bridgehead olefins (anti-Bredt olefins[12]). However, these decarbonylations were difficult to apply to 1-norbornanecarbonyl chloride (1a).[13] No trace of expected 2-norbornene was observed, and only starting material was recovered. This may be rationalized because of instability of the intermediary product, 1-norbornene (4). Molecular mechanics calculation (MM2)[14] shows that 4 [olefin strain energy[15] (OS) = 29.8 kcal/mol] is much less stable than tricyclo[5.3.1.0^{3,8}]undec-3(4)-ene (5, OS = 13.5 kcal/mol) and tricyclo[4.3.1.1^{2,5}]undec-1(9)-ene (6, OS = 15.1 kcal/mol), which were thought to intervene in the decarbonylation reaction of the corresponding bridgehead acid chlorides.[11]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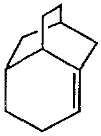
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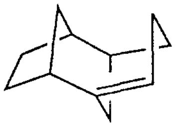
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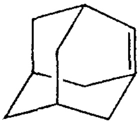
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If acylpalladium complex is formed intermediately by oxidative addition of 1a to palladium,[1a] the acylation of alkenes might be expected to occur. We have found that 1a reacts with activated alkenes to give acylated products 3 in the presence of 1 mol% of palladium catalyst and 1.2 equiv of a tertiary amine to trap hydrochloric acid formed *in situ*. The representative results are summarized in Table 1.

The following procedure for the reaction of 1a with styrene is representative (Table 1, Run 1). A mixture of 1a (1.6 g, 10 mmol), styrene (1.2 g, 12 mmol), $Pd(OAc)_2$ (22.3 mg, 0.1 mmol) and dimethylbenzylamine (1.6 g, 12 mmol) was heated at 130 °C for 4 h. The reaction mixture was treated with 1N hydrochloric acid solution and extracted two times with ether. The combined organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. The purification of the residue by column chlomatography (silica gel, hexane/ether = 20:1) followed by crystallization (hexane) gave (*E*)-β-1-norbornanoyl styrene[17] (1.0 g, 46 % yield).

Table 1. Pd-Catalyzed Acylation of Activated Alkenes with Bridgehead Acid Chlorides[a]

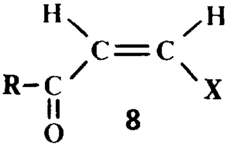
Run	Acid Chloride[b]	Activated Alkene	Catalyst	Temp [°C]	Time [h]	Product	Yield[c] [%]
1	NorCOCl	$CH_2=CHPh$	$Pd(OAc)_2$	130	4	NorCOCH=CHPh	46
2	NorCOCl	$CH_2=CHCN$[d]	$Pd(OAc)_2$	120	2	NorCOCH=CHCN	29
3	NorCOCl	$CH_2=CHCO_2Me$[e]	$Pd(OAc)_2$	115	5	$NorCOCH=CHCO_2Me$	31
4	AdCOCl	$CH_2=CHPh$	$Pd(OAc)_2$	130	3	AdCOCH=CHPh	66
5	AdCOCl	$CH_2=CHCN$[f]	$PdBr_2$	110	2	AdCOCH=CHCN	64
6	AdCOCl	$CH_2=CHCO_2Et$	$Pd(OAc)_2$	130	4	$AdCOCH=CHCO_2Et$[g]	53
7	AdCOCl	$CH_2=CHCONMe_2$	$Pd(OAc)_2$	130	12	$AdCOCH=CHCONMe_2$[h]	25

(a) All reactions were carried out in the same manner as described in the text unless otherwise stated. (b) Nor = 1-norbornyl, Ad = 1-adamantyl. (c) Isolated yields based upon the started acid chlorides. (d) 30 mmol of acrylonitrile was used. (e) 40 mmol of methyl acrylate was used. (f) Tri-*n*-butylamine was used instead of dimethylbenzylamine. (g) see ref. 16. (h) Xylene (10 ml) was used as the solvent.

The similar acylated alkenes were obtained when 1-adamantanecarbonyl chloride (**1b**) was used instead of **1a**. Adamantene (**7**, OS=38.1 kcal/mol) could not be trapped even when the reaction was performed in the presence of 2,5-dimethylfuran.[18]

The structure of **3** was confirmed by spectroscopic evidences. The observed coupling constants between the two vinyl hydrogens in ^{1}H NMR spectrum are approximately 14 Hz, which is consistent with the presence of trans vinyl hydrogens.

In all cases, the acyl groups attacked exclusively at terminal carbon atom of **2**, and the reaction proceeded stereoselectively to give acylated alkenes **3** with *E*-configuration.[19] Neither (*Z*)-isomer **8** nor alkylated product **9** could be detected by GLC analysis at any stage of these reactions. The exclusive formation of acylated alkenes **3** makes a sharp contrast to the palladium-catalyzed reaction of aroyl chlorides with activated alkenes,[20] where the arylation of alkenes (Heck-type reaction[19]) proceeds predominantly involving a highly efficient decarbonylation.



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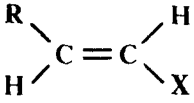

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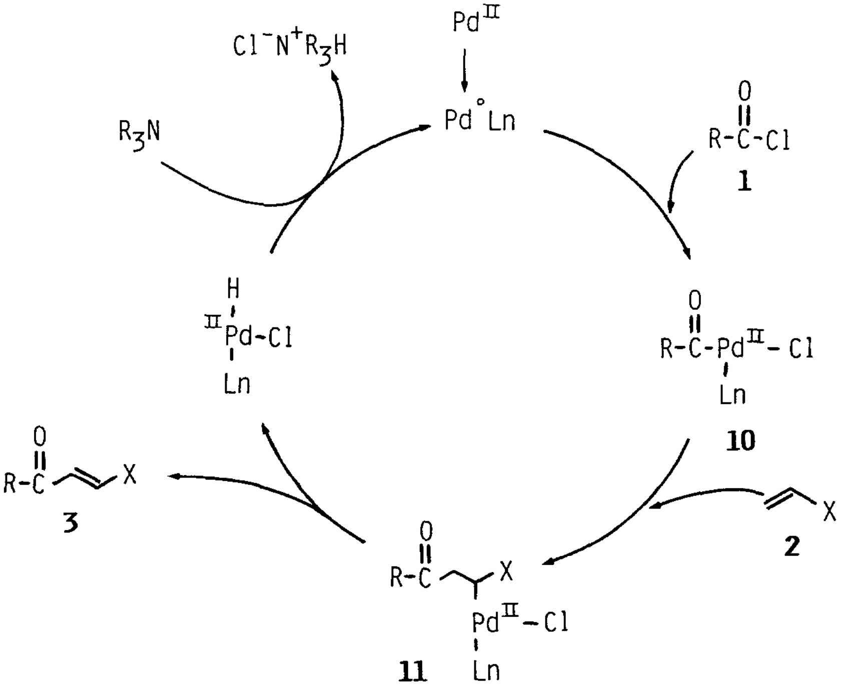
The present results may be explained by the following mechanism (Scheme 1) similar to that proposed by Tsuji et al.[2a] Oxidative addition of acid chloride to Pd(0) gives acylpalladium complex **10**, which undergoes insertion of the activated alkene resulting in alkylpalladium complex **11**. On β-elimination of palladium hydride species the complex **11** gives acylated alkene.

In conclusion, we have found that the novel palladium-catalyzed intermolecular acylation of activated alkenes occurred with bridgehead acid chlorides, which could not be decarbonylated due to the instabilities of olefins formed.

Scheme 1.



References and Notes

1. For reviews, see: (a) Tsuji, J. *Acc. Chem. Res.* **1969,** *2,* 144. (b) Stille, J. K.; Hines, L. F.; Fries, R. W.; Wong, P. K.; James, D. E.; Lau, K. S. Y. *Adv. Chem. Ser.*, **1974**, *132*, 90. (c) Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer Verlag: Heiderberg, 1980. (d) Yamamoto, A.; Yamamoto, T.; Ozawa, F. *Pure & Appl. Chem.*, **1985,** *57,* 1799.
2. (a) Tsuji, J.; Ohno, K. *J. Am. Chem. Soc.* **1968,** *90,* 94. (b) Tsuji, J.; Ohno, K. *Synthesis* **1969,** 157. (c) Tsuji, J. "Organic Synseses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, p 626.
3. (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 508. (b) Negishi, E.; Bagheri, V.; Chatterjee, S.; Luo, F.-T.; Miller, J. A.; Stoll, A. T. *Tetrahedron Lett.* **1983,** *24,* 5181. (c) Tamaru, Y.; Ochiai, H.; Sanda, F.; Yoshida, Z. *Tetrahedron Lett.* **1985,** *26,* 5529.
4. Chiusoli, G. P.; Agnes, G. *Chim. Ind. (Milan)* **1964,** *46,* 548.
5. (a) Brewis, S.; Hughes, P. R. *J. Chem. Soc., Chem. Commun.* **1965,** 489. (b) Brewis, S.; Hughes, P. R. *J. Chem. Soc., Chem. Commun.* **1966,** 6. (c) Brewis, S.; Hughes, P. R. *J. Chem. Soc., Chem. Commun.* **1967,** 71.
6. (a) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983,** *105,* 6761. (b) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985,** *107,* 8289. (c) Negishi, E.; Tour, J. M. *Tetrahedron Lett.* **1986,** *27,* 4869.
7. Larock, R. C.; Takagi, K.; Burkhart, J. P.; Hershberger, S. S. *Tetrahedron* **1986,** *42,* 375.
8. Recentry, the palladium-catalyzed reaction of benzoyl chloride with vinyltin involving insertion of norbornene has been reported; Kosugi, M.; Tamura, H.; Sana, H.; Migita, T. *Chem. Lett.* **1987,** 193.
9. (a) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982,** *104,* 3520. (b) Lai T.-W.; Sen, A. *Organometallics* **1984,** *3,* 866.
10. (a) Takaishi, N.; Takahashi, H.; Inamoto, Y. *Tetrahedron Lett.* **1985,** *26,* 2361, and references cited therein. (b) Takaishi, N.; Takahashi, H.; Yamashita, O.; Inamoto, Y. *J. Org. Chem.* **1986,** *51,* 4862.
11. Hori, K.; Ando, M.; Takaishi, N.; Inamoto, Y. *Tetrahedron Lett.* **1986,** *27,* 4615.
12. For recent reviews, see: (a) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1973,** *12,* 464. (b) Buchanan, G. L. *Chem. Soc. Rev.* **1974,** *3,* 41. (c) Keese, R. *Angew. Chem., Int. Ed. Engl.* **1975,** *14,* 528. (d) Inamoto, Y. *Kagaku (Kyoto)* **1976,** *31,* 326. (e) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; pp 117-133. (f) Shea, K. J. *Tetrahedron* **1980,** *36,* 1683.
13. Boehme, W. R. *J. Am. Chem. Soc.* **1959,** *81,* 2762.
14. (a) Allinger, N. L.; Yuh, Y. H. *QCPE* **1980,** *12,* 395. (b) Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, D.C., 1982; ACS Monogr. No. 177.
15 Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981,** *103,* 1891.
16. Kuchar, M. *Collect. Czechoslov. Chem. Commun.* **1968,** *33,* 880.
17. All new compounds gave satisfactory analytical and spectral data.
18. 1-Adamantyl chloride (37%) was obtained in addition to *N,N*-dibutyladamantanecarboxamide (18%) in the palladium-catalyzed decarbonylation of **1b** in the presence of $PdBr_2$ and tri-*n*-butylamine.
19. The similar stereochemistry has been observed in the palladium-catalyzed reactions of organic halides with alkenes; (a) Heck, R. F. *Acc. Chem. Res.* **1979,** *12,* 146. (b) Heck, R. F. *Org. React. (N.Y.)* **1982,** *27,* 345.
20. Blaser, H.-U.; Spencer, A. *J. Organomet. Chem.* **1982,** *233,* 267.

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