CHEMISTRY LETTERS, pp. 1159-1162, 1988.

Highly Selective Synthesis of Phenanthryl Acetates by Palladium Catalyzed Cyclocarbonylation of Naphthylallyl Acetates[1)]

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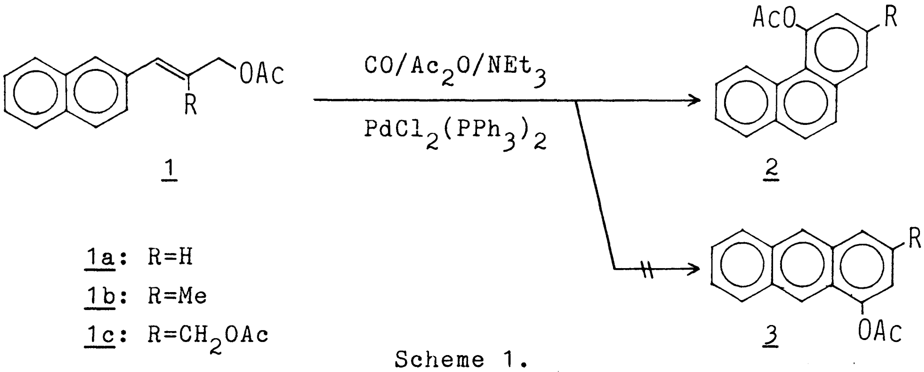
Palladium catalyzed cyclocarbonylation of 3-naphthylallyl acetates selectively affords phenanthryl acetates in good yields.

Selective formation of fused polycyclic compounds is one of the current interests in synthetic organic chemistry. Catalytic cyclocarbonylation using transition metal complexes is a promising tool for the construction of a fused polycyclic carbon skeleton, and effective syntheses of indenone, indanone, and anthraquinone by catalytic cyclocarbonylation have been reported in the literature.[2-4)] In the course of our studies on transition metal catalyzed carbonylation reactions, we have recently developed a novel palladium or platinum catalyzed cyclocarbonylation of cinnamyl compounds to afford 1-naphthol derivatives.[5,6)] In order to elucidate the applicability of the palladium catalyzed cyclocarbonylation to the synthesis of fused tricyclic aromatic systems, cyclocarbonylation of 3-naphthylallyl acetate was examined and proved to be a highly selective synthetic method of phenanthryl acetates. Here we wish to describe preliminary results.



Scheme 1.

When 3-(2'-naphthyl)-allyl acetate (1a) was carbonylated by palladium catalysts, 4-phenanthryl acetate (2a) was obtained in good yield. The typical procedure is as follows. To a 50ml stainless-steel autoclave was charged a mixture of 1a (3 mmol), $PdCl_2(PPh_3)_2$ (0.15 mmol), NEt_3 (6 mmol), Ac_2O (6 mmol), and benzene (2ml). The reactor was pressurized with CO (70 kg/cm^2 at room temperature), heated to 170 °C, and maintained at this temperature for 1.5 h with magnetic stirring. The reaction was terminated by rapid cooling and CO was discharged. The reaction mixture was washed with 10% HCl, 10% $NaHCO_3$aq, and water, dried over $MgSO_4$, and evaporated. The residual brown oil was chromatographed on silica gel to give 2a in 73% yield, which was fully characterized by IR, ^1H-NMR, ^{13}C-NMR, elemental analysis, and mp determination.[7]

Effects of catalysts on cyclocarbonylation of 1a are summarized in Table 1. In each case, 2a was the only cyclocarbonylation product and no 1-anthryl acetate (3a) was detected by GLC analysis of the reaction mixture (Scheme 1).[8] Among the catalysts examined, $PdCl_2(PPh_3)_2$ gave the best result. Other monophosphine complexes showed similar catalytic activity, although the selectivity of the reaction was considerably lower. $PtCl_2(PPh_3)_2$ was moderately effective for this reaction, while $RhCl(PPh_3)_3$, $Ru_3(CO)_{12}$-$3PPh_3$, and $Co_2(CO)_8$ showed no catalytic activity.

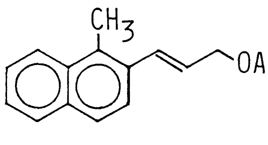
Table 1. Cyclocarbonylation of 1a[a]

Catalyst	Conversion[b] %	Yield of 2a[b] %
$PdCl_2(PPh_3)_2$	98	80
$PdCl_2(PMePh_2)_2$	99	43
$PdCl_2(PMe_2Ph)_2$	98	58
$PdCl_2(PMe_3)_2$	90	57
$PdCl_2(PCy_3)_2$	93	27
$PdCl_2(P(OPh)_3)_2$	3	3
$PtCl_2(PPh_3)_2$	22	16

a) Reaction conditions: 1a 3 mmol, catalyst 0.03 mg atom of metal, Ac_2O 6 mmol, NEt_3 6 mmol, benzene 2 ml, CO 50 kg/cm^2 at room temperature, 160 °C, 1 h.

b) Based on 1a, determined by GLC.

Results of the cyclocarbonylation of several 3-naphthylallyl acetates are shown in Table 2. In all cases, phenanthryl acetates were obtained in good yields. It is of great interest that, in the cyclocarbonylation of 1a-c, cyclization occurs selectively at the more sterically hindered α-position of the naphthalene ring, with 2a-c being the only cyclocarbonylation products. Attempted cyclocarbonylation of 3-(1'-methyl-2'-naphthyl)allyl acetate (4) did not proceed and no anthracene derivative was obtained (reaction time 3 h). This suggests that, in the reaction of 1, the intramolecular cyclization at the β-position on the naphthalene ring to form anthracene derivatives includes an unfavorable step. Conversely, 3-(1'-naphthyl)allyl acetate (5a, 5b) smoothly cyclizes at the β-position to give 1-phenanthryl acetate (6a, 6b) in fair yields.



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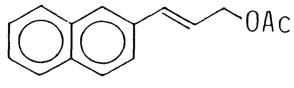
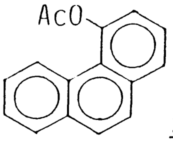
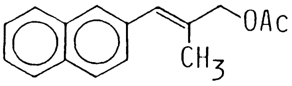
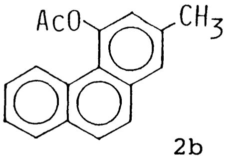
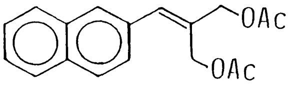
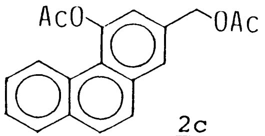
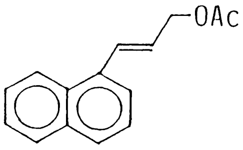
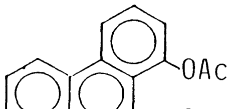
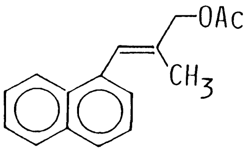
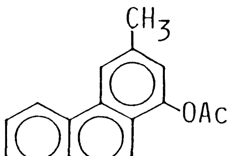
We have recently examined reactions of $Pd(CO)(PPh_3)_3$ with trans- or cis-cinnamyl bromide and discovered that their cyclocarbonylation proceeded via the intramolecular cyclization of intermediary Z-acyl complexes, trans-[(Z-$PhCH{=}CHCH_2CO)PdBr(PPh_3)_2$] and/or trans-[(Z-$PhCH_2CH{=}CHCO)PdBr(PPh_3)_2$].[9] It seems plausible that cyclocarbonylation of 1a also proceeds via the cyclization of Z-acyl complexes such as 7, which are formed by the oxidative addition of 1a to a Pd(0) species, CO insertion to form E-acyl complexes, and the subsequent carbon-carbon double bond isomerization. Cyclization of 7 at the α-position presumably generates a palladium complex 8 and consecutive elimination affords

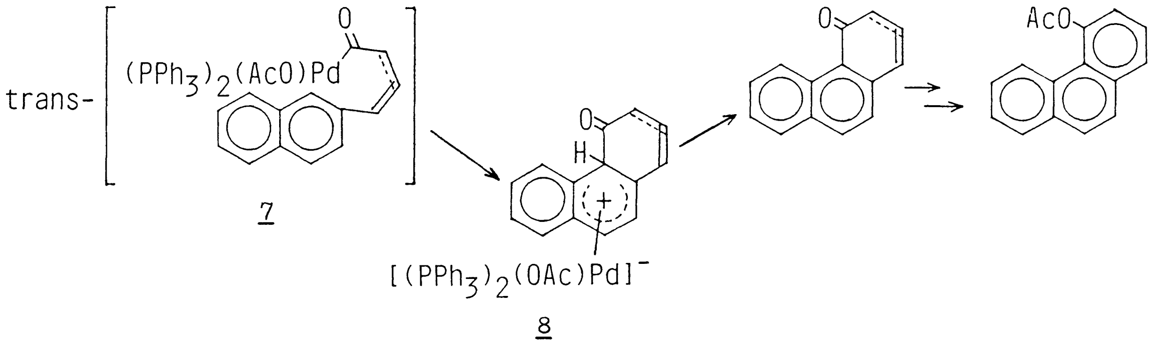
Table 2. Phenanthryl Acetates from 3-Naphthylallyl Acetates[a]

Substrate	Reaction time/h	Product	Isolated yield/%
 1a	1.5	 2a	73
 1b	3.0	 2b	76
 1c	3.0	 2c	64
 5a	1.5	 6a	50
 5b	3.0	 6b	70

a) For reaction conditions, see text.

phenanthrenone, which is transformed into 2a by keto-enol isomerization and acetylation (Scheme 2). To date, mechanistic details of the intramolecular cyclization of acyl complexes such as 7 are not clear. Palladation of naphthalene is known to occur at the β-position,10) while the cyclocarbonylation of 1 proceeds at the α-position. Therefore palladation is not included in the present cyclocarbonylation. At present the cyclization of acyl complexes are tentatively interpreted as proceeding via electrophilic attack at the aromatic ring. Generally, the α-position of the naphthalene system is more subject to electrophilic attack than the -position. Therefore, if the present cyclocarbonylation includes an intramolecular electrophilic attack by the acyl group, the observed α-selectivity to give 2 is reasonable.

In conclusion, the present reaction provides a potential method for the preparation of functionalized phenanthrene derivatives whose selective synthesis is hardly attainable by substitution reactions of phenanthrene or traditional Haworth synthesis. Application of this cyclocarbonylation reaction to construct other polycyclic systems including heterocycles is now under investigation.



Scheme 2.

This work was partially supported by a Grant-in-aid for Scientific Research No.62607505 from the Ministry of Education, Science and Culture.

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7) 2a: ^{1}H-NMR(CDCl$_3$, δ); 2.55(s, 3H), 7.33(dd, 1H, J=7.6 Hz, 1.2 Hz), 7.56-7.65 (m, 3H), 7.73(s, 2H), 7.81(dd, 1H, J=7.9 Hz, 1.2 Hz), 7.89 (dd, 1H, J=6.6 Hz, 2.1 Hz), 9.10(dd, 1H, J=7.3 Hz, 2.1 Hz). IR(cm^{-1}, KBr); 1757($\nu_{C=O}$), 1220 (ν_{COC}). Found: C,81.34; H,5.12%. Calcd for $C_{16}H_{12}O_2$: C,81.26; H,5.10%. mp (°C); 60.3-61.5(lit. 58-60; H.M.Duvall, E.Mosettig, J.Am.Chem.Soc., 60, 2409(1938)).

8) The absence of 3a in the reaction mixture was confirmed by comparison of the gas chromatogram of the reaction mixture with that of an authentic sample of 3a which was independently prepared by a literature method (R.E.Schmidt, Chem.Ber., 37, 66(1904); H.Dienel, Chem.Ber., 38, 2862(1905)).
3a: ^{1}H-NMR(CDCl$_3$, δ); 2.55(s, 3H), 7.25(d, 1H, J=7.3Hz), 7.42-7.50(m, 3H), 7.91(dd, 1H, J=8.5 Hz, 0.6Hz), 7.99-8.03(m, 2H), 8.43(s, 1H), 8.47(s, 1H). IR(cm^{-1}, KBr); 1759($\nu_{C=O}$), 1212(ν_{COC}). mp(°C); 134.1-135.7(lit. 129-130; H.E.Fierz-David, L.Blangey, and H.Streiff, Helv.Chim.Acta, 29, 1718(1946)).

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(Received April 15, 1988)