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A NEW TYPE OF FUNCTIONAL GROUP DIFFERENTIATION IN PALLADIUM-CATALYZED REACTIONS

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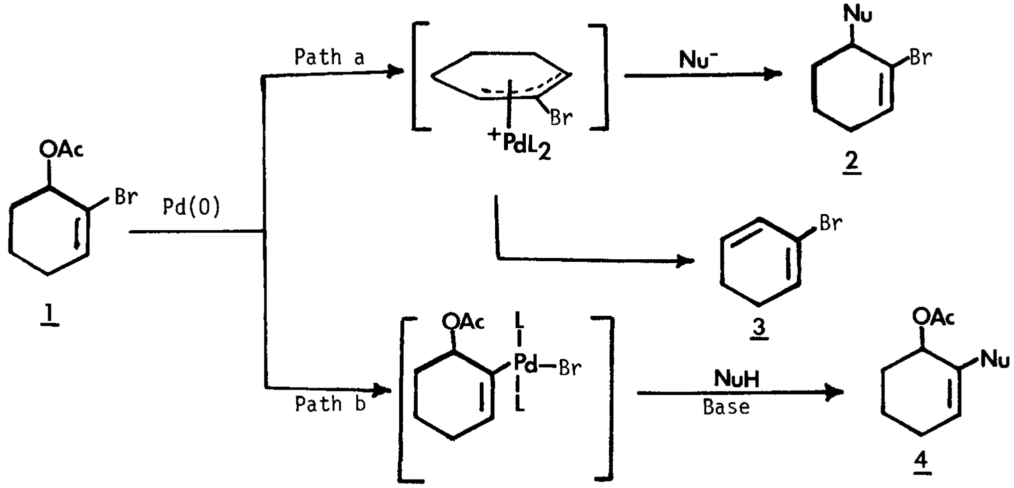
Abstract: Products of palladium-catalyzed ethynylations of various 2-bromoallyl acetates show that the formation of σ-vinylpalladium intermediates, instead of π-allylpalladium complexes, is preferred in such substrates.

Palladium-catalyzed nucleophilic alkylations of simple allyl acetates by way of π-allylpalladium complexes[1] and the coupling of aryl or vinyl halides with nucleophiles through σ-vinylpalladium intermediates[2] are well-known reactions. For 2-haloallyl acetates (e.g. 1, Scheme 1) which bear both the allyl acetate and vinyl bromide moieties such that they affect each other, palladium-catalyzed reaction could lead to any or all of the product types 2, 3 or 4 through the two probable reaction pathways a and b. We did not find any previous report concerning this type of chemoselectivity in palladium-catalyzed reactions of substrates like 1.



Scheme 1

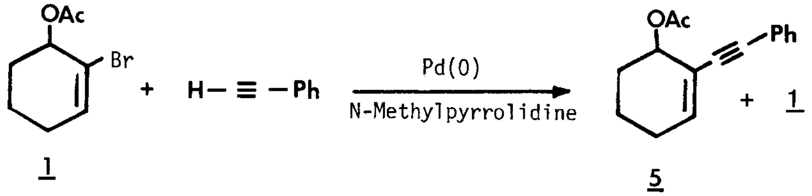
We report here that various 2-bromoallyl acetates, under palladium-catalyzed reaction conditions, reacted with acetylenes according to path b only. No product types expected from a π-allylpalladium intermediate, like 2 or 3 for substrate 1 in Scheme 1, were observed.

Refluxing a solution of 10 mmol of 2-bromo-3-acetoxycyclohexene 1[3], 2 mol % of various palladium catalyst systems (Table 1) and 15 mmol of phenylacetylene in 10 mL of N-methylpyrrolidine for 6-8 h gave 24-42% of the acetylene-coupled product 5 and some unreacted bromoacetate 1 only (Eq. 1).

Table 1. Palladium-catalyzed Ethynylation of 2-Bromo-3-acetoxycyclohexene 1.

Catalyst ( )[a]	Yield %[b]	
	5	Recovered 1
$Pd(OAc)_2/PPh_3$ (1:2)	24	47
$(PPh_3)_2PdCl_2/CuI$ (2:1)	25	45
$(PPh_3)_4Pd$	42	27

(a) Mol ratio (b) Of isolated compounds, not optimized.



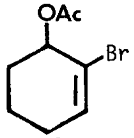
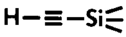
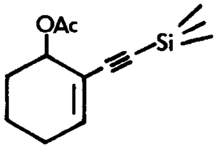
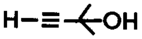
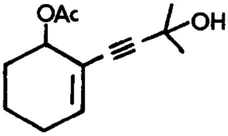
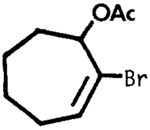
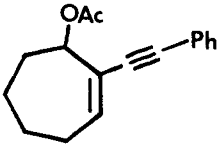
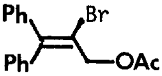
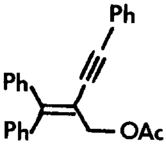
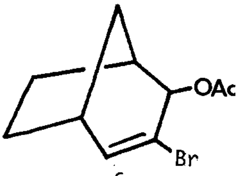
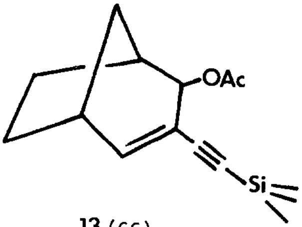
Eq. 1

Other examples of this chemoselectivity are given in Table 2. Tetrakis(triphenylphosphine)palladium(0) was used for all reactions on the table except for Entry 2 for which $(PPh_3)_2PdCl_2/CuI$ gave a better result.

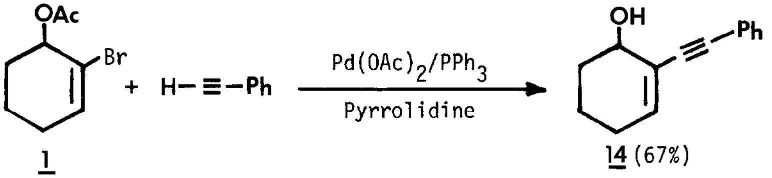
Verification of the absence of a π-allylpalladium intermediate in these reactions was based on the fact that in the absence of a nucleophile, a π-allylpalladium complex should undergo elimination to give a diene.[7] With 1 under this reaction condition, elimination should afford 2-bromocyclohexadiene 3 (Scheme 1). When 1 was refluxed in N-methylpyrrolidine for 6 h with 2 mol % of $(PPh_3)_2PdCl_2$ and 1 mol % of CuI only, it was recovered unreacted in 91%. Recovery of unreacted substrate was also high in reactions with unreactive acetylenes (see Entry 4, Table 2). These very high recoveries of 2-bromoallyl acetates under conditions that favor elimination in simple allyl acetates are consistent with the absence or insignificance of the π-complex reaction route in these reactions.

We obtained further evidence of the unusual reactivity of 2-haloallyl acetates from their palladium-catalyzed reactions in pyrrolidine. For example, refluxing 1 with phenylacetylene in pyrrolidine using 2 mol % of $Pd(OAc)_2$ and 4 mol % of PPh_3 for 2-4 h gave the enynol 14 in 67% (Eq. 2). Repeating the reaction without the acetylene resulted in the isolation of the

Table 2. Palladium-catalyzed Ethynylation of 2-Bromoallyl Acetates.

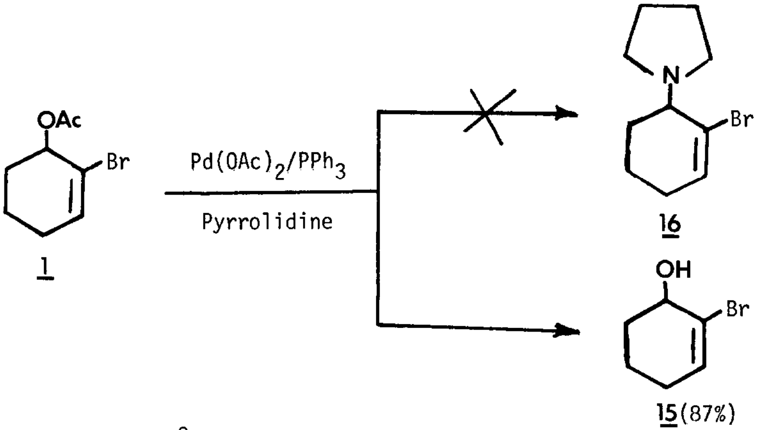
Entry	Substrate	Acetylene	Reaction Time(h)	Product[4] (%)[a]	Recovered Substrate (%)[a]
1[b]	 1[3]		3	 6 (47)	15
2	1		4	 7 (26)	27
3	 8[3]	H—≡—Ph	0.7	 9 (81)[5]	0
4	8		12	--	93
5	 10[3]	H—≡—Ph	1.5	 11 (32)	48
6[b]	 12[6]		15	 13 (66)	22

(a) Isolated compounds, yields not optimized (b) Reaction in a sealed tube at 80°C.



Eq. 2

bromoalcohol 15[8] in 87% yield. The amination product 16, which would be expected from a π-allylpalladium intermediate,[9] was not observed.



The above results represent the first examples of this type of chemoselectivity in palladium catalyzed reactions. They also implicate an unusual effect of a 2-halosubstituent on the ease of fission of the allylic carbon-oxygen bond in allyl acetates.

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References and Notes

1. Trost, B.M., Tetrahedron, 32, 2615 (1977).
2. Heck, F.R., Dieck, H.A., J. Organomet. Chem., 93, 259 (1975).
3. Sandler, S.R., J. Org. Chem., 32, 3876 (1967).
4. All new compounds had correct chemical analyses (elemental or high resolution mass spectral). For 11: mp 146-7°C; ^{1}H NMR(CCl_4): δ 7.20(m, 15H), 4.80(s, 2H), 2.00(s, 3H); Calc'd for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 84.92; H, 5.64.
5. 2-(Phenylethynyl)cyclohepta-1,3-diene, a secondary product from 9 was also obtained in 16%. Its quantity depended on reaction time. For example, after 3 h, it was isolated in 60% while 9 was obtained in 40% yield.
6. Prepared in 52% yield overall from norbornylene by refluxing its dibromocarbene adduct, prepared according to: Moore, W.R., Moser, W.R., LaPrade, J.E., J. Org. Chem., 28, 2200 (1963), in glacial AcOH/NaOAc.
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