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A PALLADIUM MEDIATED REDUCTIVE CYCLIZATION

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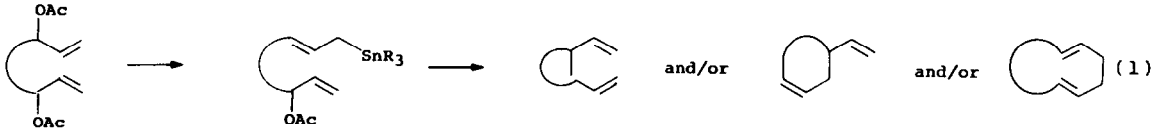
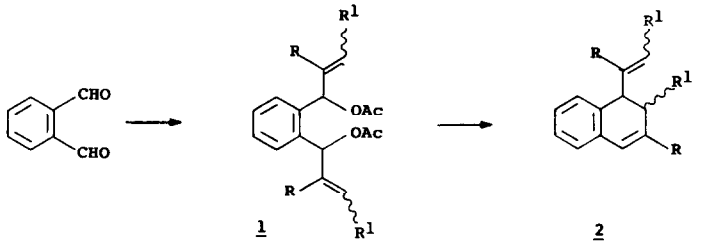
SUMMARY: α,ω-bis(Allylic acetates) undergo regioselective intramolecular reductive coupling with hexamethyldistannane catalyzed by Pd(O).

The versatility of allyl carboxylates as electrophilic partners in formation of C-C bonds has increased substantially from the ability to activate the C-O bond with transition metal templates.[1] The ability to invert the reactivity of allyl acetates from electrophiles to nucleophiles by conversion to allyl silanes[2] and stannanes,[3] mediated by transition metal templates, combined with our early observation of cross-coupling[4] of allylstannanes and allyl acetates[4a] suggests a new cyclization as outlined in eq. 1.



(1)

To test the feasibility of this approach, a THF solution of the α,ω-bis(allyl acetate) 1a, easily available from o-phthaldehyde, was refluxed with 1 eq. of hexamethyldistannane, 5 mol% of palladium acetate, 25 mol% of triphenylphosphine, and an excess of 1-hexene (to generate the active Pd(o)

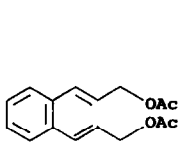


(2)

a) R=R1=H b) R=CH3, R1=H c) R=H, R1=Ph

catalyst).[5] A single product emerged in 83% isolated yield (eq. 2). Structure 2a[6] derived from the spectral data and especially the ^{1}H [δ7.0-7.2, m, 4H; 6.44, bd, J=10 Hz, 1H ; 5.95, m, 2H; 5.07, bd, J=8.5 Hz, 1H; 5.01, bd, J=17 Hz, 1H; 3.47, q, J=8 Hz, 1H ; 2.48, dddd, J=17.5, 7.3, 4.5, 2.0, 1H; 2.29, dddd, J=17.5, 8.9, 4.5, 2.0, 1H] and ^{13}C[δ 140.6, d; 135.8, s; 133.5, s; 127.7, d; 127.2, d;

126.9, d; 126.8, d; 126.2, d; 115.2, t; 42.1, d; 29.5, t] nmr spectra. Following the reaction by tlc revealed the presence of several intermediates, one of which was isolated and identified as the isomerized bis(acetate) 3.



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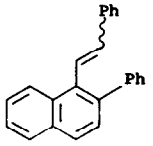
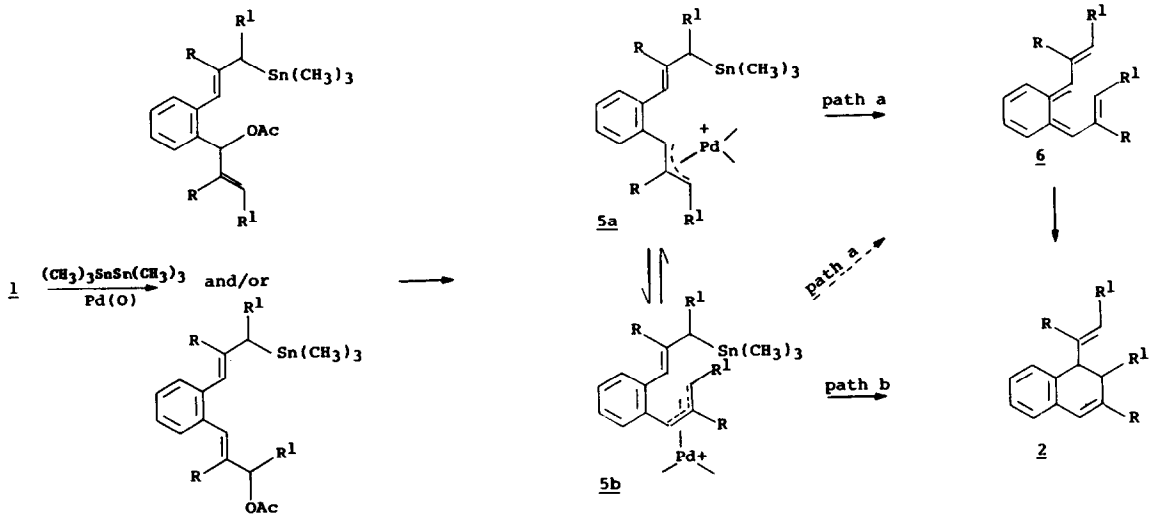


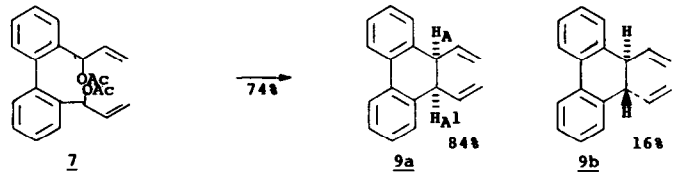
4

The regioselectivity of the coupling showed no sensitivity to substituents. Thus, both 1b and 1c (eq. 2) also gave the 1-vinyl-1,2-dihydronaphthalenes 2b[6] and 2c[6] in 52 and 71% yields respectively. Because of the presence of stereoisomers, 2c was further characterized by aromatization (DDQ, PhH) to 4. While the mechanistic pathway is not established, two pathways can be envisioned to account for the regioselectivity as outlined in eq. 3.[7] The routes differ in that one envisions a direct coupling of the allylstannane with the

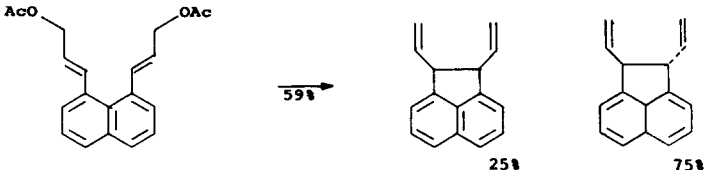


π-allylpalladium intermediate 5 (path b) and the other invokes an o-quinodimethide such as 6 (path a).

To test whether an o-quinodimethide was an obligatory intermediate, the biphenyl system 7 and acenaphthyl system 8 were investigated. Both participated smoothly in the reductive coupling under standard conditions. While an extended analogue of an o-quinomethide is possible in the case of 7 although it is



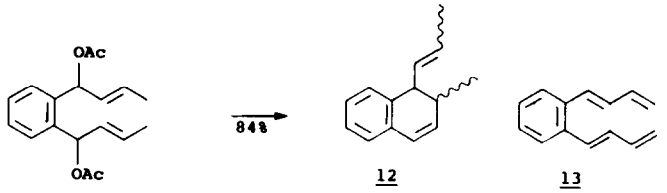
7 9a 9b



8 10a 10b

sterically rather unlikely, such a species is impossible in the case of 8. The high regioselectivity presumably reflects the preference to form six and five member rings over eight or ten and seven or nine member rings respectively. Tentatively, the major isomer of 9[6] is assigned as cis based upon the vicinal coupling constant $J_{AA'}$=3.4 Hz as determined from the ^{13}C satellites in the proton spectrum, the higher field of this proton in the ^{1}H nmr spectrum (δ 3.53 vs 3.61), and the lower field of the benzylic carbon in the ^{13}C nmr spectrum (δ 48.98 vs 45.16). The ^{1}H (major δ4.48, minor δ4.05) and ^{13}C (major δ52.94, minor δ56.15) criteria suggests the reverse assignment for 10.[6]

The crotyl system 11 tests the efficiency of the cyclization. The major



11 12 13

product was the bis-eliminated species 13 rather than the cyclization product 12. The preferential elimination reflects the ineffectiveness of the distannane as a stannylation reagent--a problem that may be overcome with more effective stannylating conjunctive reagents.[3] If the problem arose in the coupling step, then a dihydroanalogue of 13 would have been formed.

The mildness of the reaction conditions and the high regioselectivity commend this procedure for the synthesis of delicate systems as exemplified by dihydronaphthalenes. The ease of availability of the requisite substrates and their unreactivity in the absence of the metal catalyst enhance the potential of this approach in synthesis.

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5. An in situ Wacker[1] reaction of 1-hexene serves as a convenient source of an active Pd(o) catalyst. Any other source of Pd(o) catalyst presumably also is applicable.

6. Full spectral characterization and elemental composition via high resolution mass spectroscopy was obtained. Regioisomeric coupling products have not been detected.

7. For a discussion of the mechanism of stannylation see ref. 3 and of the coupling see ref. 4. Presumably, the same mechanisms are involved here. Under the reaction conditions, the allylstannane would also likely be in dynamic allylic equilibrium so that, regardless of the regiochemistry of coupling, either isomer can arise by allyl inversion with respect to the allylstannane.

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