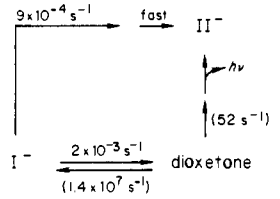
Y) of II⁻ and an increase in that of III⁻ and the % Y of K· equals approximately twice that of III⁻ (Table I).[13] At saturation in K⁻, II⁻ and III⁻ form through competing parallel first-order reactions rate-controlled by k_{sp} and k_1, respectively. The maximum yield of III⁻ that may be obtained may then be calculated as 100 $k_1/(k_1 + k_{sp})$ = 73%. In the presence of K⁻, the dioxetane is partitioned to III⁻ and $\{II^-\}^*$ by parallel and competing (k_4 vs. $k_3[K^-]$) first-order reactions. Since the quantum yield (Φ) is proportional to the percent yield of $\{II^-\}^*$, it follows that % Y of II⁻/% Y of III⁻ = $\alpha\Phi$/% Y of III⁻ = $k_4/k_3[K^-]$. The fact that dioxetane partitions between $\{II^-\}^*$ and trapping by K⁻ is established by a plot (Figure 2) of Φ/(% Y of III⁻) vs. $1/[K^-]$ which is linear with the zero intercept as required. The slope of the plot of Figure 2 is equal to $k_4/\alpha k_3 = 4.1 \times 10^{-9}$ M.

In conclusion, we have established that the reactions of Scheme I account for the modes of decomposition of I⁻ in *t*-BuOH (anhydrous, O_2-free) in the presence of *t*-BuOK in excess over reactants. The constants k_{sp} and k_1 have been determined directly, and with the assumption that k_3 represents a thermodynamically favorable electron transfer ($k_3 \simeq 10^9$ M^{-1} s^{-1}) and a knowledge of the fluorescence quantum yield of $\{II^-\}^*$,[11] we arrive at the approximation of eq 3. In eq 3 the rate constants have not been



(3)

corrected for the extent of ionization of intermediates and pertain, therefore, to the experimental conditions employed.[9] Under the conditions of this study, the rate constant for dioxetane formation is twice that for the Criegee rearrangement (path C). Even though dioxetane formation involves an intramolecular nucleophilic attack by an α-effect base, the strain brought about by formation of a four-membered ring and the forcing of an unfavorable eclipsed conformation upon the nonbonding electrons of the peroxide oxygen atoms disfavor this process.[14] Thus, conversion of dioxetane back to I⁻ is associated with a rate constant of $\sim 10^7$ s^{-1}, so that the rate of rearrangement through the Criegee mechanism is $\sim 10^5$ faster than through the diioxetane pathway. It is our plan to extend this study to other solvent conditions and to other α,β-unsaturated hydroperoxides.

Acknowledgment. This work was supported by grants from the National Institutes of Health and the National Science Foundation.

(13) The yields of K·, II, and III were determined as follows: [K·] was quantified by using its absorbance at 730 nm (ϵ_{730} = 680 M^{-1} cm^{-1}: Muto, S.; Bruice, T. C. J. Am. Chem. Soc. **1980**, *102*, 4472). The yields of II and III were determined by high-performance LC. The LC analyses were carried out with a Du Pont Instruments reverse-phase column (Lichrosorb 5RP 8, 25 cm, 4.6 mm) with CH_3CN–H_2O, 40:60 (v/v), at a flow rate 1.2 mL/min. The products were monitored at 242 nm (=λ_{max} of I, II, and III). Retention times of authentic I, II, and III were 11.9, 25.2, and 10.1 min, respectively.

(14) O'Neal, H. E.; Richardson, A. H. *J. Am. Chem. Soc.* **1970**, *92*, 6553.

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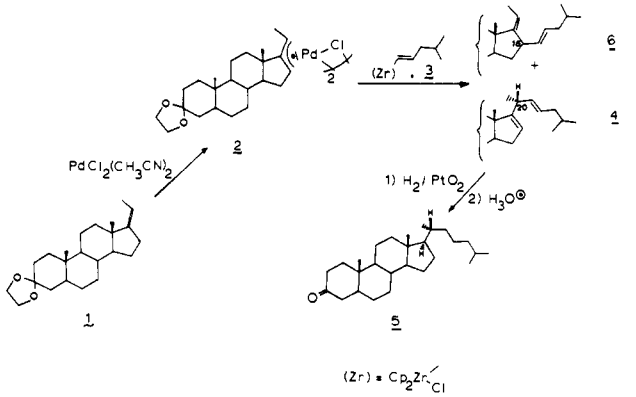
Regiocontrolled Coupling of (π-Allyl)palladium Complexes with Organozirconium Species: A New Steroid Synthesis

Sir:

Allylic functionalization of olefins, achieved through the intermediacy of (π-allyl)palladium complexes, has been elegantly applied in high-yield regio- and stereoselective syntheses of a variety of target molecules in which the key bond-forming step has been regarded as a direct attack by a nucleophile on the allylic ligand.[1] For carbon–carbon bond formation, the scope of these procedures is constrained by the limited range of permissible carbon nucleophiles: it is reported that, in general, only stabilized anions can be used.[2] Trost has applied this synthetic methodology to problems in steroid synthesis[3] in which the stabilized carbanion is the precursor of the steroid side chain formed by attack on a (π-allyl)palladium complex derived from a simpler olefin containing the steroid nucleus. Because of stereochemical preferences of substituents in this π-allylic complex and the requirement for trans attack of the nucleophile upon it, the steroidal products thus formed have the epi configuration at C-20.[4] Were it possible to utilize these simple olefin-derived (π-allyl)palladium complexes in a process involving attack by a carbon species *at the metal*, followed by C–C reductive elimination, steroids containing the natural *R* configuration at C-20 would result. Indeed, regiocontrolled attack (with respect to the termini of the allylic unit) to couple modifiable side chains with accessible π-allylic complexes derived from simple steroidal olefins would achieve convergent syntheses of a wide variety of steroidal analogues having the natural configuration at C-20. Alkenylzirconium complexes had been shown[5,6] to transfer alkenyl groups to Pd(II) salts, and we now report that these alkenylzirconium species couple with (π-allyl)palladium chloride complexes to give high yields of the resultant 1,4-dienes. We wish to describe these results in the context of regioselective synthesis of steroids possessing the natural configuration at C-20.

Olefin **1** was converted (90%) to (π-allyl)palladium chloride dimer **2**[7,8] by refluxing with excess $PdCl_2(CH_3CN)_2$ in methylene



chloride in the presence of sodium carbonate. Initial attempts at coupling **2** and **3**[9] did not proceed smoothly to give the desired diene **4**. Rather, a complex mixture was obtained consisting of **1**, **4**, and the regioisomer **6** corresponding to coupling at C-16. The combined yield of coupled product was 59% (**4**:**6** formed in a ratio 2:3).

It was hoped that formation of **1** could be suppressed and that regiocontrolled coupling could be obtained by equilibrating **2** with

(1) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.

(2) Trost, B. M.; Weber, L.; Strege, P.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3426.

(3) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 3435.

(4) Transformation of $\Delta^{17(20)}$ olefin to an allylic acetate enabled preparation of steroidal material with the natural configuration at C-20 using a catalytic amount of $(PPh_3)_4Pd$.

(5) Yoshifuji, M.; Loots, M. J.; Schwartz, J. *Tetrahedron Lett.* **1977**, 1303.

(6) Okukado, N.; Van Horn, D. E.; Klima, W. L.; Negishi, E. I. *Tetrahedron Lett.* **1977**, 1027.

(7) ^1H NMR (C_6D_6) δ 3.59 (s, 4), 3.37 (q, 1, J = 7.6 Hz), 3.32 (br d, 1, J = 2.7 Hz), 1.20 (d, 3, J = 7.6 Hz), 0.9–2.1 (br m, 20), 0.62 (s, 6).

(8) ^{13}C NMR shows **2** to be a single compound. The data of D. N. Jones and S. D. Knox (*J. Chem. Soc., Chem. Commun.* **1977**, 165) suggest that strong shielding of the C-18 methyl group would be expected if the Pd were on the β face of the steroid. No such shift is observed. The pertinent features of the proton NMR are in good agreement with data reported by Trost for the syn isomer of bis[chloro[16,17,20-η^3-3-methoxy-19-norpregna-1,3,5-(10),17(20)-tetraene]palladium(II)].[3]

(9) For a general procedure to prepare this type of complex, see: Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

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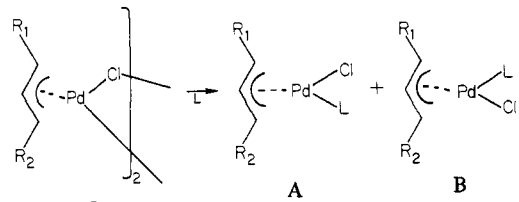
Table I. Effect of Added Ligands on Regioselectivity (4:6)[a]

ligand	equiv added[b]	4:6 ratio in coupled product
none		0.67
PPh_3	4.1	1.0
	13.2	1.0
PPh_2(*o*-anisyl)	4.6	1.0
tri-*o*-tolylphosphine	2.7	0.9
	14.2	0.3
$PMePh_2$	4.0	1.0
$P(OMe)_3$	4.6	1.0
pyridine	4.0	0.7
maleic anhydride	2.1	1.5
	4.1	1.5
	2.9	1.8[c]
	2.8	6.0[d]
	3.0	>7.0[e]

[a] All reactions performed at room temperature unless otherwise noted. [b] Per Pd. [c] 0 °C. [d] -40 °C. [e] -78 °C.

Scheme I



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added ligand prior to addition of **3**.[10,11] Initially, the effects of phosphine ligands on the reaction in THF were examined (Table I). It is notable that the addition of phosphines did *not* result in control of the regiochemistry of coupling in a pattern which could be correlated with the steric bulk of the phosphine.[11] Variation in solvent (CH_3CN, CH_2Cl_2, toluene, or hexane) also had little effect on this regiochemistry. However, as shown in Table I, equilibrating **2** with maleic anhydride prior to addition of **3** gave mixtures of coupled products in which **4** predominated. For example, equilibration of **2** (1.0555 g, 2.175 mmol) with maleic anhydride (0.5345 g, 5.454 mmol)[12] in 250 mL of dry, air-free THF under N_2 at -78 °C, followed by slow addition of a cooled solution of **3** (1.0 g, 2.9 mmol in 50 mL THF, also at -78 °C), blocked formation of **1** and gave **4** and **6** in a ratio of at least 7:1 as determined by ^1H NMR. Purification via liquid chromatography on silica gel, eluting with ethyl acetate/hexane, gave a 96% combined yield of coupling product as a viscous oil from which **4** was isolated (78%) by crystallization followed by high-performance LC separation of the mother liquors (recrystallization from EtOAc/EtOH, mp 92-93 °C).[13]

Diene **4** was hydrogenated using PtO_2/EtOAc at 3 atm of H_2 for 40 h. The saturated ketal was recovered in quantitative yield[14] and hydrolyzed by refluxing in aqueous 1,2-dimethoxyethane, acidified with sulfuric acid. The product was purified by liquid chromatography (silica gel, ethyl acetate/hexane) and recrystallized from ethanol (mp 128-129 °C). Its spectral properties (^1H, ^{13}C NMR) were identical with those of an authentic sample (mmp 128-129 °C), confirming that the compound formed possesses the natural steroidal configuration at C-20.[15]

The formation of **4** (with the *R* configuration at C-20) proves that alkylation at Pd precedes C-C bond formation. The origin of regiocontrol by added ligand of this coupling reaction is believed to result from a geometrical preference of the (π-allyl)(ligand)PdCl precursor, A or B (Scheme I).[16] In this scheme, transmetalation to A or B results in replacement of -Cl by the alkenyl group and is followed by rapid reductive elmination of product. We propose that steric differences between R_1 and R_2 give rise to a distortion of the π-allylic ligand in **2** by movement of Pd closer to the sterically less congested terminus. This perturbed geometry dictates the preferred ligated complex (A or **B**) depending on the donor/acceptor properties of that ligand,[17,18] hence establishing regiocontrol in these "syn" coupling reactions.

The scope of this reaction as a synthetic procedure is now under examination, and further investigation of the origin of regiocontrol is proceeding.[19]

Acknowledgment. We gratefully acknowledge support for this research provided by the National Science Foundation, Grant No. CHE-79-00996.

(10) We suggest that (allyl)Pd-R can readily undergo β-hydrogen transfer from R to Pd, leading to formation of olefin. Coordination of ligands such as maleic anhydride should suppress this β-hydrogen transfer and hence olefin byproduct formation. It is significant to note that dimethylcadmium, in which the possibility for β-H transfer to Pd is obviated, can be used to couple methyl groups with π-allylic palladium species: Castanet, Y.; Petit, F. *Tetrahedron Lett.* **1979**, 3221.

(11) The regiochemistry of (anti) nucleophilic attack on (π-allyl)Pd complexes in the presence of phosphines has been related to the steric bulk of the added ligand. Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.

(12) Numata, S.; Kurosawa, H. *J. Organomet. Chem.* **1977**, *131*, 301.

(13) ^{13}C NMR shows **4** to be a single compound: ^1H NMR ($CDCl_3$) δ 5.22-5.42 (m, 3), 3.91 (s, 4), 2.78 (br m, 1), 1.0-2.0 (m, 23), 1.07 (d, 3, J = 8 Hz), 0.88 (s, 3), 0.81 (s, 6), 0.75 (s, 3). Diene **6** was obtained by preparative high-performance LC: ^1H NMR (C_6D_6) δ 5.41 (br m, 3), 3.58 (s, 4), 3.13 (br m, 1), 1.70 (d, 3, J = 7.0 Hz, of finely split d), 1.2-2.3 (br m, 23), 0.94 (s, 3), 0.88 (2s, 6), 0.71 (s, 3).

(14) The Δ^{16} monoolefin was recovered if hydrogenation was stopped after 2 h. ^1H NMR ($CDCl_3$) shows vinylic resonance as a multiplet at δ 5.18-5.26.

(15) Nair, G. V.; Mosettig, E. *J. Org. Chem.* **1962**, *27*, 4659.

(16) Numata and Kurosawa[11] have inferred the existence (in solution) of such geometrical isomers (L = tertiary phosphine) from ^1H NMR data.

(17) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(18) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350.

(19) Preliminary investigations reveal that a variety of Pd(II) or Pd(0) complexes can serve as precursors of catalysts for coupling allylic halides or acetates and alkenylzirconium species: Hayasi, Y.; Temple, J. S.; Schwartz, J., unpublished results.

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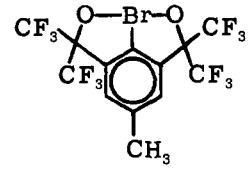
A Dialkoxyarylbrominane. The First Example of an Organic 10-Br-3 Species[1]

Sir:

We report the isolation and characterization of the first organobrominane, dialkoxyarylbrominane **1**, a 10-Br-3 species of



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surprising stability. Although analogous iodine species have long been known, with a variety of substituent types,[2] all reported 10-Br-3 species, such as BrF_3, $Br(NO_3)_3$,[3] $Br(OSO_2F)_3$,[4] and $Br(OSeF_5)_3$,[5] contain fluorine or other very electronegative inorganic ligands.

(1) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Algria, A.; Kochi, J. K. *J. Am. Chem. Soc.*, in press. They describe the classification scheme applied here to a 10-electron bromine species with three ligands to bromine (10-Br-3).

(2) (a) Agosta, W. C. *Tetrahedron Lett.*, **1965**, *31*, 2681. (b) Baker, G. P.; Mann, F. G.; Sheppard, N.; Tetlow, A. J. *J. Chem. Soc.* **1965**, 3721. (c) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 1542. Koser, G. F.; Wettach, R. H.; Smith, C. S. *Ibid.* **1980**, *45*, 1544.

(3) Schmeisser, M.; Brandle, K. *Angew. Chem.* **1961**, *73*, 388.

(4) Roberts, J. E.; Cady, G. H. *J. Am. Chem. Soc.* **1960**, *82*, 352.

(5) Seppelt, K. *Chem. Ber.* **1973**, *106*, 157.

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