

CHARACTERIZATION OF SOME σ -BONDED PALLADIUM COMPLEXES BY OXIDATIVE CLEAVAGE WITH COLLINS' REAGENT

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SUMMARY

Oxidation of allylpalladium chloride complexes or other σ -bonded organopalladium complexes with Collins' reagent affords carbonyl compounds in fair to good yield. Norbornenylpalladium complexes afford both norbornenone and nortricyclenone derivatives under these conditions.

Oxidation of allylpalladium complexes with Cr^{VI} has been reported to afford carbonyl compounds in low yield¹. We have found that Collins' reagent² (dipyridine-chromium(VI) oxide) is a superior oxidant for this purpose, and converts C-Pd bonds into ketones or aldehydes, typically in 40–60% yield.

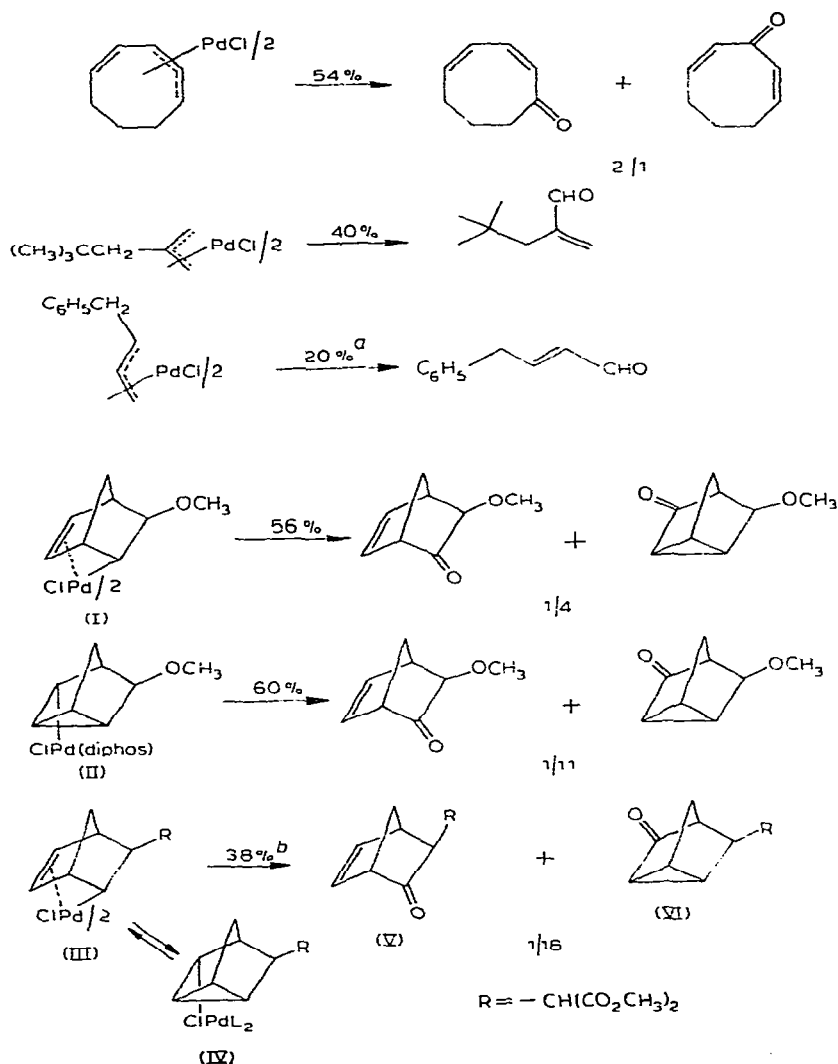
PREPARATION OF σ -BONDED COMPLEXES

The allyl complexes³, the methoxynorbornenyl complex I⁴, and the methoxynortricyclyl complex II⁵ were prepared by known methods. Synthesis of III was accomplished from the sodium salt of dimethylmalonate and norbornadiene-palladium dichloride in tetrahydrofuran, but the crude complex slowly deposited palladium upon standing* and was used immediately without characterization.

OXIDATIVE CLEAVAGE

In general, the complex to be oxidized is treated with a 10-fold excess of Collins' reagent in methylene chloride for 2 h at 25°. All sites which are capable of σ -bonding to palladium are subject to oxidation. Thus, cyclooctadienylpalladium chloride dimer affords both 2,7-cyclooctadienone and 2,4-cyclooctadienone⁷, while either I or II affords a mixture of 5-methoxynortricyclenone and 3-methoxy-5-norbornen-2-one (Scheme 1). In the latter case, it is not known whether partial equilibration of bicyclic and tricyclic complexes occurs prior to oxidation^{5,8}, or whether skeletal rearrangement occurs at a later stage of reaction involving some

* A previous attempt⁶ to prepare III resulted in material which decomposed at 0°.



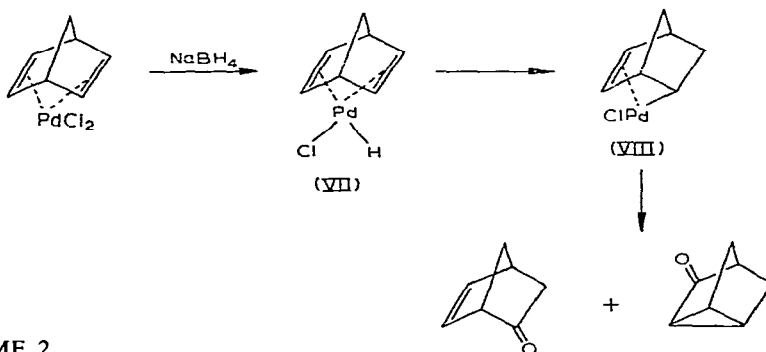
SCHEME 1. (a) The other possible oxidation product, benzyl vinyl ketone, was not detected. However, this may be the result of decomposition of the highly reactive ketone. (b) Overall yield from norbornadiene-palladium dichloride.

oxidized intermediate*. Similarly, the complex III (which may equilibrate with IV**) affords bicyclic and tricyclic ketones, assigned structures V and VI on the basis of NMR, IR, and mass-spectral data.

* Jones oxidation of norbornenol does not afford rearranged nortricyclenone. However, Jones oxidation of norbornenylborane is analogous to oxidation of the palladium complexes in that both norbornenone and nortricyclenone are formed⁹.

** The NMR spectrum of crude III contains vinyl hydrogen signals at δ 6.1–6.4 (br) which disappear upon addition of pyridine. A corresponding increase in the integral between 1 and 2 δ is noted, indicating formation of IV (L = pyridine) from the bicyclic complex. This behavior is characteristic of norbornenyl-palladium complexes⁸.

Oxidative cleavage may be used to characterize organopalladium complexes which cannot be isolated in crystalline form. Thus, reduction of norbornadienepalladium dichloride at -40° with a deficiency of sodium borohydride in the presence of excess norbornene to minimize overreduction⁸ affords an organopalladium intermediate which we have been unable to purify. This substance is formulated as the norbornenylpalladium chloride complex VIII on the basis of its conversion into norbornene, norbornane, and nortricyclene upon further reduction*.



SCHEME 2

Oxidation of the presumed intermediate VIII with Collins' reagent (Scheme 2) affords nortricyclenone and norbornenone in a ratio of 1/1, as expected from the analogous behavior of I, II, and III. If the reduction-oxidation sequence is repeated using sodium borodeuteride instead of sodium borohydride, the resulting nortricyclenone contains 0.9 D in a ratio of ca. 2/1 of *syn/anti* deuterium (NMR analysis⁸) relative to the carbonyl group. This result is compatible with predominant *endo* hydride (or deuteride) transfer, presumably via a palladium hydride complex such as VII in the initial reduction step. Competition from *exo* hydride or deuteride transfer by an unknown pathway leads to the minor deuterated product *anti*-5-deuterio-3-nortricyclenone.

EXPERIMENTAL

General oxidation procedure

Dry dipyrindine chromium(VI) oxide² (10 mmol) was dissolved in dry methylene chloride (40 ml, distilled from P₂O₅). To this solution was added the palladium complex (1 mmol) dissolved in dry methylene chloride (5 ml) in one portion. Immediate reaction occurred, resulting in a dark, gummy precipitate. The reaction mixture was stirred with a mechanical stirrer for 2 h at 25° at which time the methylene chloride was decanted. The semisolid residue was triturated with methylene chloride and the combined CH₂Cl₂ fractions were washed with water, dried over MgSO₄, and evaporated under a Vigreux column at atmospheric pressure. The products were

* The ratio of norbornene:norbornane:nortricyclene is 9/7/1 in the presence of 2,3-dicarbomethoxy-5-norbornene as diborane trap⁶.

analyzed and isolated by GLPC, or in the case of III, by preparative layer chromatography over silica gel.

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