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Preliminary communication

ADDITION OF KETONE ENOLATES TO π-ALLYLPALLADIUM COMPOUNDS. STEREOCHEMISTRY AND SCOPE OF THE REACTION

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Summary

Conditions have been developed for the addition of ketone enolates to π-allylpalladium systems. A stereochemical study has shown that the enolate adds from the face of the π-allyl system opposite to palladium.

Palladium promoted nucleophilic addition of malonates to π-allyl systems has found extensive application in organic synthesis, especially following the discovery that allylic acetates react catalytically in the presence of palladium(0) [2]. If less stabilized carbanions could be used, the potential of the reaction would be greatly increased.

We have now found that ketone enolates can be added to π-allyl systems. The success of the reactions depends strongly on the conditions. The best results so far obtained were with the π-cyclohexenyl system 1. When an excess of triphenylphosphine (4 mol of phosphine/palladium) is added to a solution of the complex 1 in tetrahydrofuran (THF), immediately followed by four equivalents of the potassium enolate of acetone, *cis*-3-methoxy-6-(2-oxopropyl)-cyclohexene (2) is formed in about 60% yield. In analogous reactions with the π-butenyl complex 3 mixtures of the unsaturated ketones 4 and 5 are obtained. The yields are 4 6%, 5 7% (R = CH_3). With R = Ph, the yields are improved, 4 51%, 5 20%.

The mechanism of the reaction is indicated by the stereochemistry of the product. The enolate could add either as an external nucleophile to the π-allyl system (path a) or first coordinate to palladium, then yield the observed products by reductive elimination (path b). In the former case (a), the enolate would add from the face opposite to palladium, and in the latter case (b) from the same face.

The stereochemistry of 2 was determined by analysis of its NMR spectrum

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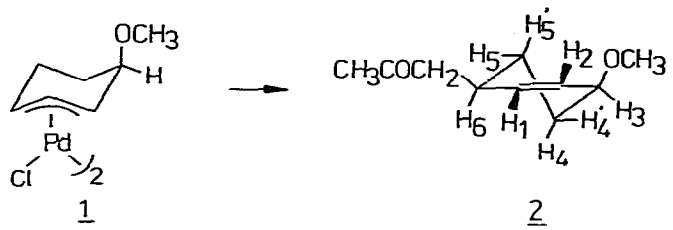

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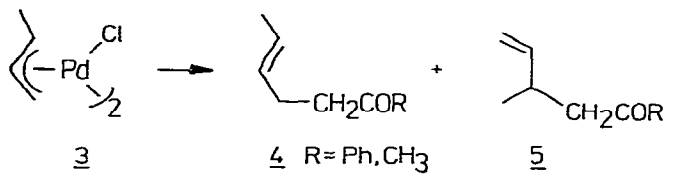
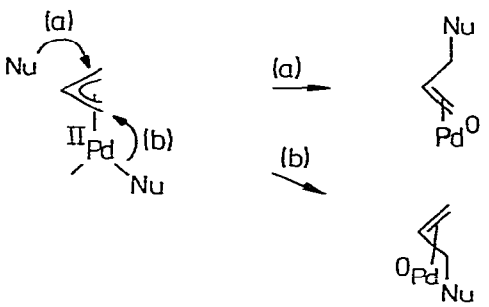


3 4 R = Ph, CH_3 5



and by comparison with related 3,6-disubstituted cyclohexenes [3,4]. A primary indication of a *cis* relationship between the two substituents of 2 is the fact that the four methylene protons H(4), H(4′), H(5) and H(5′) form a single multiplet at δ 1.7 ppm, whereas related *trans* compounds frequently exhibit two well resolved multiplets around δ 2 and 1.5 ppm. Furthermore, the average couplings J(H(3)H(4)) and J(H(3)H(4′)) are low, 3.5 and 4 Hz, and the sum of J(H(6)H(5)) and J(H(6)H(5′)), which could not be resolved, is large, 15 Hz. Taken together with the values for the coupling constants J(H(1)H(6)) (2 Hz), J(H(1)H(3)) (~0), J(H(2)H(3)) (4 Hz), and J(H(2)H(6)) (1.8 Hz) (cf. ref. 5), this strongly suggests that product 2 has a 3,6-*cis*-configuration. In addition, it has in solution the predominant configuration in which the methoxy is axial and the 2-oxopropyl group equatorial. In compound 1, the methoxy group and palladium are attached to opposite faces of the π-allyl system [4]. The enolate thus adds as an external nucleophile by path (a), in analogy with additions of malonates [6] and amines [3a] but in contrast to additions of hydride [4] or phenyl carbanion [7], which react according to path (b).

It seemed possible that the enolate, by analogy with dimethylamide [8] might be reluctant to react according to path (b), and that this could be a reason for the low yields of 4 and 5 from the π-butenylpalladium chloride (3).

We therefore treated the complex 3 with either the silyl ether of acetophenone, an established route to oxa-π-allyl complexes [9], or the mercury

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complex **6**. An unstable complex **7** appeared to form. On heating, a high yield of acetophenone was formed, probably by proton abstraction from the methyl group of the π-butenyl system. It thus appears that for high yields of the desired coupling products, e.g. **4** and **5**, the enolate must be prevented from coordinating to palladium to favour direct attack on the π-allyl system.

Although the yield of coupling products still is low for the π-butenyl complex **3**, the success with the π-cyclohexenyl system **1** is encouraging, particularly since this reaction is an example of stereospecific introduction of two functional groups, one of which is a ketone, into a 1,3-diene system.

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