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Pd(II)-MEDIATED COUPLING OF 1,1-DIMETHYL-2-PROPYNYL ACETATE WITH ITSELF AND 1-DECENE

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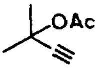
Abstract: Heating 1,1-dimethyl-2-propynyl acetate (1) with $PdCl_2(MeCN)_2$ (0.05 - 0.1 mol equiv) and MeCN alone afforded (*E*)-2,7-dimethylocta-2,4,6-trien-3,6-diyl diacetate (2) (yield *ca.* 20%) and with 1-decene (7 mol equiv) present (*E*)-2-methyltetradeca-2,4-dien-3-yl acetate (7) (30%) together with 2 (12%).

This letter describes two exploratory experiments that suggest Pd(II)-vinylcarbene complexes derived from 1,1-dimethyl-2-propynyl acetate (1) as intermediates in novel apparent carbene-carbene[1] and carbene-alkene[2] couplings. The couplings with the alkene are intermolecular variants and the self-coupling an extension of recently developed cyclizations.[3]

In the first experiment, 1 (20 mmol) was heated (60°C, 17 h) with $PdCl_2(MeCN)_2$ (1 mmol) solubilized with MeCN (1 ml) under Ar. Distillation of the resulting mixture at 12 Torr to remove low-boiling material and then at 0.01 Torr (200°C, Kugelrohr), afforded a complex mixture containing (*E*)-2,7-dimethylocta-2,4,6-trien-3,6-diyl diacetate (2) [mp 144 - 145°C, air-sensitive] as the main component (*ca.* 2 mmol), together with 1-formyl-2-methyl-1-propenyl acetate (3), 3-methyl-2-butenylidene diacetate (4) (0.3 and 0.1 mmol) and an unknown compound[4] as minor components plus a large number of trace components. The low-boiling fraction contained MeCN, 1, 3-methyl-2-butenal (5), and $MeCO_2H$. 2 was isolated by crystallization from hexane and the other products by preparative GC. The yields given are estimates based on GC analysis of the distilled mixture.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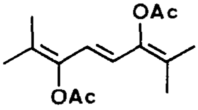
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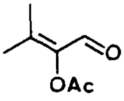
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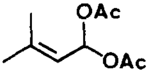
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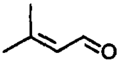
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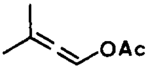
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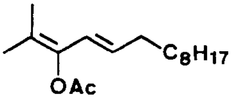
In the second experiment, the same reagents [1 (10 mmol), $PdCl_2(MeCN)_2$ (1 mmol), MeCN (1 ml)] were heated (60°C, 19 h) in 1-decene (70 mmol) under Ar. In the same way as before were now obtained (*E*)-2-methyltetradeca-2,4-dien-3-yl acetate (7) and 2 as the main products (1.5 and 0.6 mmol), together with (*E*)-2,5-dimethyltrideca-2,4-dien-3-yl acetate (9), its (*Z*)-isomer (10) (0.2 mmol of each), and an unknown compound as minor products, plus again numerous trace products. Among the latter, 3, 4, and the (*Z*)-isomer (8) of 7 were identified by GC/MS coupling.[5]



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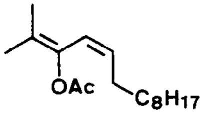

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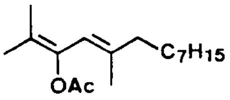

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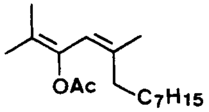

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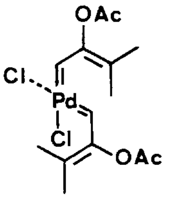
It may be speculated that 2 is formed from a bisvinylcarbene complex such as 11[1] and 7 - 10 from a vinylcarbene-1-decene complex such as 12,[3] the complexes arising by chelation and acetate migration.[3] Other mechanisms for the reactions with 1-decene can be envisaged,[3] but extension of these to the self-coupling is cumbersome. The reactions with 1-decene in addition require Pd(II)-mediated migrations of a H-atom from C-1 to C-2 of the alkene or vice versa. 4 and 5 must be derived from 3-methylbuta-1,2-dienyl acetate (6) formed by Pd(II)-catalyzed rearrangement of 1. Catalysis of this rearrangement by Pd(II) is new but its catalysis by Cu(I) and Ag(I) is well-established.[6]



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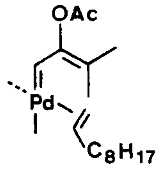

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References and Notes

1. For a review and a theoretical study, see C.N. Wilker, R. Hoffmann and O. Eisenstein, *Nouv. J. Chim. 7*, 535 (1983), and references therein.

2. The couplings 1 + 1-decene → 7 - 10 can be classified as cooligomerizations. For a review of this field, see W. Keim, A. Behr and M. Röper, in 'Comprehensive Organometallic Chemistry', vol. 8, chapter 52, ed. G. Wilkinson, Pergamon, Oxford, 1982.

3. V. Rautenstrauch, *J. Org. Chem. 49*, 950 (1984).

4. Tentatively identified as 6-chloro-2,7-dimethylocta-2,4,6-trien-3-yl acetate.

5. There were also traces of a fifth component isomeric with 7 - 10.

6. R.C. Cookson, M.C. Cramp and P.J. Parsons, *J. Chem. Soc., Chem. Commun. 1980*, 197, and references therein.

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