Preparation of 1,5-Dienes by Photolysis of η^3-Allylpalladium Complexes

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Summary 1,5-Dienes are formed in good yields when dilute solutions of η^3-allylpalladium complexes in acetonitrile are irradiated at 366 nm.

THE use of η^3-allylpalladium complexes in organic synthesis has been extensively investigated over the past few years.[1] However, there has been no report on the photochemical behaviour of these compounds. From the photoreactivity of many organometallic complexes, it was expected that radical coupling reactions might be observed with η^3-allylpalladium complexes. We report here that 1,5-dienes are the main products formed when acetonitrile solutions of η^3-allylpalladium complexes are irradiated.

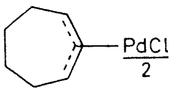
In a typical experiment a carefully deoxygenated solution of di-μ-chloro-bis[1—3-η-cycloheptenylpalladium] (**1**) (150 mg) in MeCN (60 ml) was irradiated at 366 nm for 2 h. Precipitation of palladium was observed and owing to the resulting filter effect, filtration through Florisil and re-irradiation were necessary to obtain a 52% conversion. The 1,5-diene (**7**) (87% yield), and unchanged starting material were isolated from the reaction mixture. Similarly the dienes (**8**)—(**12**) were produced from complexes (**2**)—(**6**) (Table).

TABLE[a]

Substrate	Conversion/%	Product	Isolated yield/%
(**1**)	52	(**7**)	87[b]
(**2**)	100	(**8**)	55[c]
(**3**)	78	(**9**)	32[d]
(**4**)	80	(**10**)	80[b,e]
(**5**)	62	(**11**)	78[b,f]
(**6**)	39	(**12**)	96[b]

[a] The starting complexes were prepared according to H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 225 and B. M. Trost, P. E. Strege, L. Weber, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, 1978, **100**, 3407. Irradiation was carried out using 2.5—6 mM l^{-1} of substrate in MeCN under argon with light of wavelength λ 366 nm. [b] Satisfactory i.r., n.m.r., and mass or microanalytical data were obtained. [c] Identified by comparison with authentic material (see P. de Mayo, J. B. Stothers, and W. Templeton, *Can. J. Chem.*, 1961, **39**, 488). [d] Identified by comparison with literature data (see M. Kolobielski and H. Pines, *J. Am. Chem. Soc.*, 1957, **79**, 5820). [e] Obtained as a mixture of 1,5-dienes with the head to head dimer predominating. [f] The major product (62% yield) appears to result from head to head coupling.

Other functions, such as acetate or even a conjugated enone, do not interfere with the dimerization of the allylic group, which seems to be very regioselective. These results contrast with those reported for the photolysis of nickel complexes. Whereas the coupling of η^3-allyl nickel complexes to give 1,5-dienes under thermal conditions in the presence of CO or phosphines is well known,[2] dimers are formed as only very minor products in the photolysis of these complexes.[3] The recent report on radicals and hexa-1,5-diene formation during the photolysis of tetra-(η^3-allyl)-complexes of molybdenum, tungsten, zirconium, and hafnium[4] suggests that homolytic cleavage of the carbon–palladium bond might be involved in the reaction of η^3-allylpalladium complexes. Further work, now in progress, is required before the mechanism can be defined exactly.



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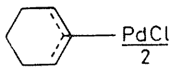

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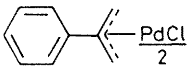

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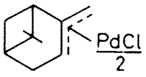

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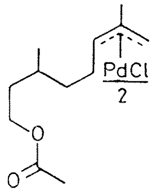

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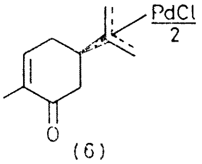

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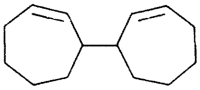
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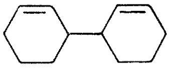
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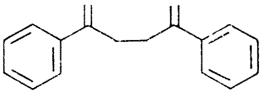
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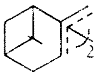

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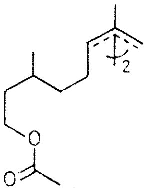

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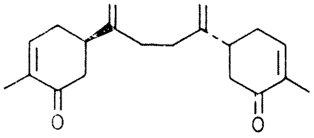

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[4] R. Benn and G. Wilke, *J. Organomet. Chem.*, 1979, **174**, C 38.