Preparation of Conjugated Carbonyl Compounds by Photolysis of η^3-Allylpalladium Complexes

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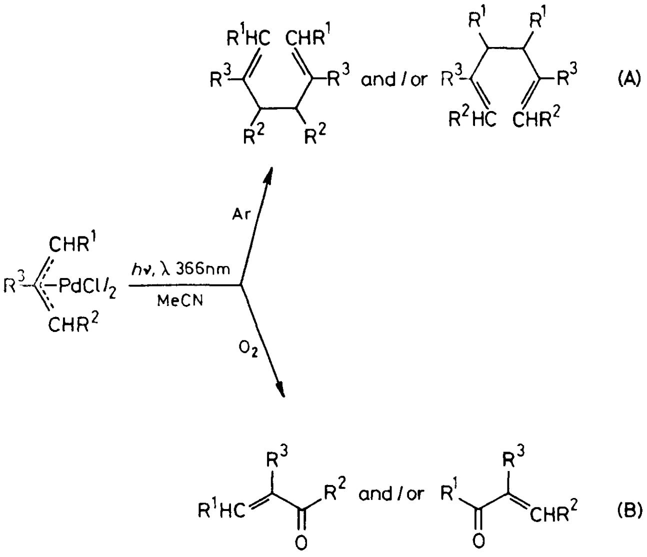
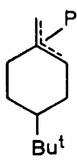
Summary Irradiation at 366 nm of oxygenated solutions of η^3-allylpalladium complexes leads to unsaturated carbonyl compounds.

Recently, we described a general synthesis of 1,5-dienes by photolysis of carefully deoxygenated solutions of η^3-allylpalladium complexes[1] (reaction A). This photoreaction was efficiently quenched by traces of oxygen; the irradiation of oxygenated solutions of the same starting materials led mainly to conjugated carbonyl compounds (reaction B). As shown by our previous work[1] as well as by the results reported here both reactions appear to be general.

In a typical experiment, a solution of the complex (**1**) (528 mg) in MeCN (140 ml) was irradiated under oxygen at 366 nm for 9·5 h. After evaporation of the solvent, distillation yielded 1-formyl-4-t-butylcyclohexene (**8**) (136 mg) containing less than 5% of 2-methylene-5-t-butylcyclohexanone. Chromatography on silica gel of the distillation residue gave unchanged starting material (176 mg). Similarly, the αβ-unsaturated ketones or aldehydes (**9**)—(**16**) were produced from the complexes (**2**)—(**7**) (Table).

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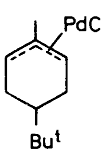
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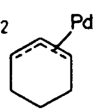
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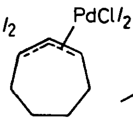
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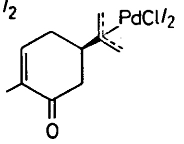
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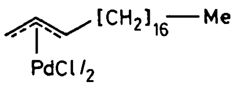
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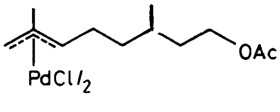
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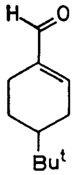
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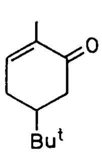
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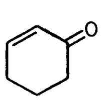
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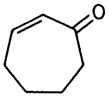
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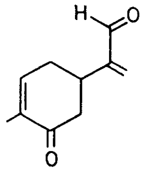
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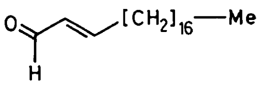
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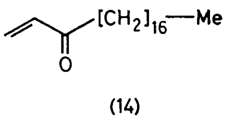
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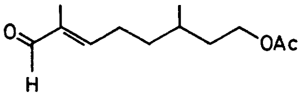
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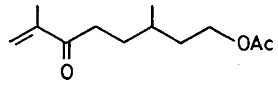
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These results are very different from those reported by Hojabri[2] who observed only the formation of decomplexed alkenes on irradiation of either oxygenated or deoxygenated ethanolic solutions of η^3-allylpalladium complexes.

TABLE.[a]

Substrate	Conversion/%	Product	Yield/%[b]
(**1**)	66	(**8**)[c]	68
(**2**)	100	(**9**)[d]	37
(**3**)	81	(**10**)[d]	48
(**4**)	64	(**11**)[d]	55
(**5**)	76	(**12**)[c]	26
(**6**)	100	(**13**)[c]	39
		(**14**)[c]	32
(**7**)	86	(**15**)[c]	27
		(**16**)[c]	29

[a] The starting complexes were prepared according to the method of M. Sakakibara, Y. Takahashi, S. Sakai, and Y. Ishii *Chem. Commun.*, 1969, 396; B. M. Trost, P. E. Strege, L. Weber, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, 1978, **100**, 3407. Irradiations were carried out using 1·5—22 mM solutions of substrate in MeCN [except for (**6**): CH_2Cl_2–MeCN, 3:2–v/v] under oxygen with light of wavelength 366 nm. [b] Isolated yield based on unrecovered starting material; purity > 95% (t.l.c. and/or g.l.c.; n.m.r.). [c] Satisfactory i.r., n.m.r., and mass spectral data were obtained. [d] Identified by comparison with authentic material.

Our procedure allows the oxidation of η^3-allylpalladium complexes under milder conditions than other described methods;[3] further work aimed at controlling the regioselectivity of this photoreaction is underway.

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[2] F. Hojabri, *J. Appl. Chem. Biotechnol.*, 1973, **23**, 205.

[3] D. M. Jones and S. D. Knox, *J. Chem. Soc., Chem. Commun.*, 1975, 166; E. Vedejs, M. F. Salomon, and P. D. Weeks, *J. Organomet. Chem.*, 1972, **40**, 221; P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, 1971, Vol. 1, pp. 236—238; Vol. 2, pp. 122—123.