

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

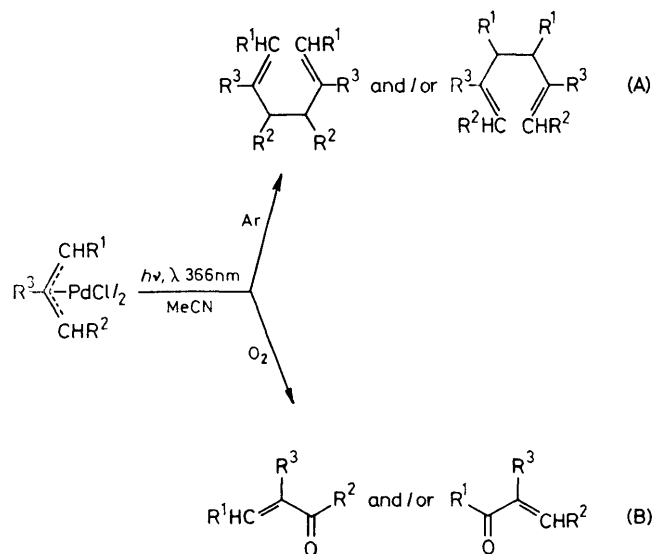
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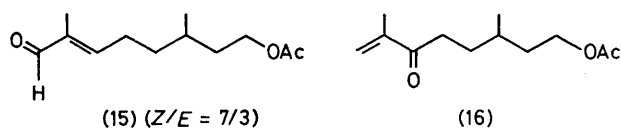
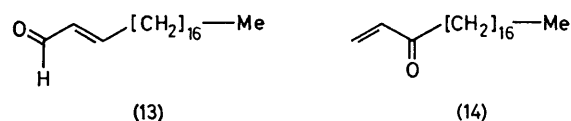
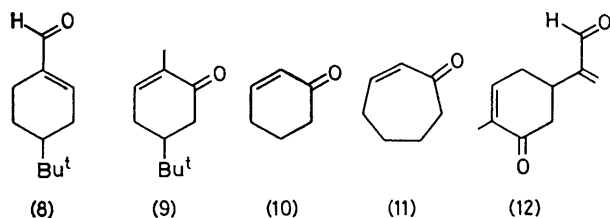
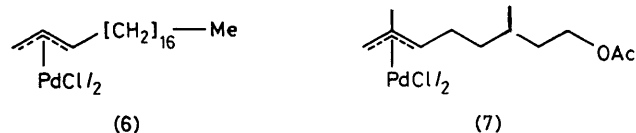
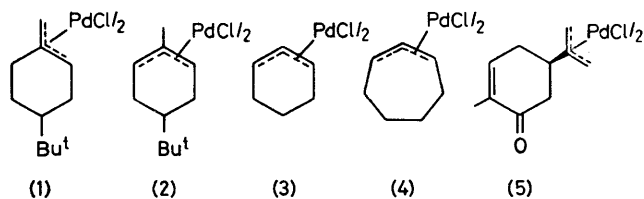
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Summary Irradiation at 366 nm of oxygenated solutions of η^3 -allylpalladium complexes leads to unsaturated carbonyl compounds.

RECENTLY, we described a general synthesis of 1,5-dienes by photolysis of carefully deoxygenated solutions of η^3 -allylpalladium complexes¹ (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 work¹ 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 $\alpha\beta$ -unsaturated ketones or aldehydes (**9**)—(**16**) were produced from the complexes (**2**)—(**7**) (Table).





These results are very different from those reported by Hojabri² 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	Con- version/%	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): CH₂Cl₂-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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¹ J. Muzart and J. P. Pete, *J. Chem. Soc., Chem. Commun.*, 1980, 257.

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.