Tetrahedron Letters,Vol.23,No.35,pp 3577-3578,1982 0040-4039/82/353577-02$03.00/0
Printed in Great Britain

PHOTOACTIVATION OF ALKENE OXIDATION BY MOLECULAR OXYGEN IN THE PRESENCE OF PALLADIUM

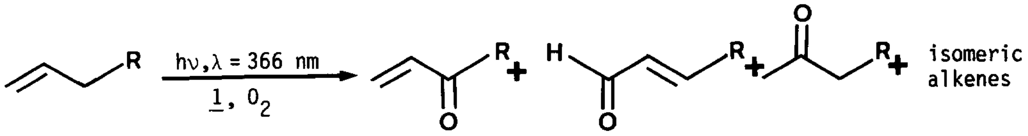
Jacques MUZART[*]*, Patrick PALE and Jean-Pierre PETE*

Laboratoire de Photochimie, Equipe de Recherche Associée au C.N.R.S.
"Réarrangements thermiques et photochimiques", U.E.R. Sciences,
51062 Reims Cedex, France.

Summary A catalytic cycle which leads to α-β ethylenic ketones and methyl ketones from terminal alkenes in the presence of palladium trifluoroacetate,oxygen and U.V. light is described.

Catalytic oxygenation of organic compounds has found wide application in synthesis[1-3]. Recently, we found that α,β-unsaturated ketones were produced by photolysis of η^3-allylpalladium chloride complexes under an oxygen atmosphere[4]. This efficient and mild oxidation can be considered as a method for converting alkenes into enones ; however, two steps and a stoechiometric amount of palladium are needed. In order to realize a one pot reaction with a catalytic cycle, $Pd(OCOCF_3)_2$ 1, which easily abstracts allylic or enolic hydrogens[5,6] was considered to be a possible valuable catalyst under an oxygen atmosphere.

In fact, irradiation of a solution of eicosene 2a in anhydrous solvents, in the presence of 1 (2.5 moles %) and under an oxygen atmosphere leads to α,β-ethylenic carbonyl compounds 3a, 4a and to the methyl ketone 5a. However, migration of the double bond of the starting alkene, which is well-known in the absence of U.V. light[7] is the major observed pathway (table).



2 3 4 5

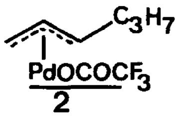
a : R = $C_{17}H_{35}$ b : R = C_9H_{19} c : R = C_5H_{11}

Table

Alkene	Solvent	Time	Catalyst	Conversion %	Isomerised alkene %,a	3 + 4		5	
						%,a	%,b	%,a	%,b
2a	MeCN +CH_2Cl_2	27 h	1	68	47	2.5	100	7.5	300
2a	Me_2CO	20 h	1	59	10	6.5	250	14	540
2a	MeCN +CH_2Cl_2	19 h	6	52	20	4.3	170	10	400
2a	Me_2CO	19 h	6	27	5	2.4	95	4.7	185
2b	Me_2CO	23 h	1	57	30	8.1	325	10.8	430
2c	MeCN	22 h	1	c	c	2	80	10	405

a : *yields calculated from starting alkene* ; b : *yields relative to the catalyst* ;
c : *not calculated.*

As shown in the table, the efficiency of this reaction changes with the nature of the solvent. This oxidation procedure seems to be general for terminal alkenes. Furthermore, use of the preformed η^3-allylpalladium trifluoroacetate complex 6 as catalyst leads to similar mixtures.



6

As anhydrous conditions are used, formation of peroxidic palladium complexes in the photolytic mixture could explain, at least in part, the presence of the methyl ketone among the oxidized products[3,8]. It should be noted that in the absence of U.V. light, no methyl ketone was detected.

Acknowledgments : This work was supported by the C.N.R.S., "ATP, Chimie Fine". P.P. thanks the D.G.R.S.T. for a research grant.

References

1. G. READ and P.J.C. WALKER, J.C.S. Dalton, 883 (1977).
2. R.A. SHELDON and J.K. KOCHI, Advances in Catalysis, Acad. Press, vol. 25, p.273 (1976).
3. H. MIMOUN, Pure Appl. Chem., 53, 2389 (1981).
4. J. MUZART, P. PALE and J.P. PETE, J.C.S. Chem. Comm., 668 (1981).
5. B.M. TROST and P.J. METZNER, J. Amer. Chem. Soc., 102, 3572 (1980).
6. J. MUZART and J.P. PETE, J. Molec. Catalysis, 15, 373 (1982).
7. P.M. MAITLIS, The Organic Chemistry of Palladium, Acad. Press, vol. 2, p.128 (1971).
8. H. MIMOUN, R. CHARPENTIER, A. MITSCHLER, J. FISCHER, R. WEISS, J. Amer. Chem. Soc., 102, 1047 (1980).

(Received in France 18 June 1982)