Reactions of Ketoximes with Tetrakis(triphenylphosphine)palladium. Palladium-induced Beckmann Fragmentation of Ketoximes

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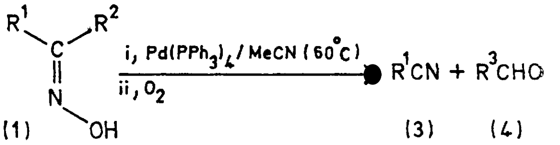
Summary A novel palladium-induced Beckmann fragmentation of ketoximes to give nitriles and aldehydes, by reaction with tetrakis(triphenylphosphine)palladium and molecular oxygen, is described.

Recently transition metal-induced carbon–carbon bond fissions have been extensively studied in olefin methatheses,[1] isomerizations of small ring compounds,[2] and skeletal rearrangements of dienes.[3] We now report a novel palladium-induced carbon–carbon bond fission of ketoximes to give nitriles and aldehydes under neutral and mild conditions.

Treatment of the ketoximes (**1a**—**e**) with tetrakis(triphenylphosphine)palladium (**2**) and then molecular oxygen under mild conditions gives the nitriles (**3**) and aldehydes (**4**) (Scheme). This reaction corresponds to strong acid-induced[4] or photochemical[5] Beckmann fragmentations of ketoximes which, unlike aldoximes, can be converted into nitriles only with difficulty.

A typical procedure for the reaction is as follows. A mixture of β-benzil mono-oxime (**1a**) (5 mmol) and (**2**) (25 mmol) in dry MeCN was stirred for 2 h at 60°C under argon. To the resulting yellow suspension molecular oxygen was introduced until a homogeneous dark-brown solution was obtained. After stirring for a further 5 h at 60 °C, filtration followed by distillation gave PhCN (85%) and PhCHO (43%). Other examples of formation of nitriles from ketoximes are summarized in the Table. The best yields were obtained with oximes of aromatic diketones. The reaction does not take place with aliphatic ketoximes, although oximes of dibenzyl ketones can be converted into the corresponding benzylnitriles in 20—30% yield along with the formation of PhCN (30%) and deoximated



(1) (3) (4)

(1a) (β) R^1=Ph, R^2=C(O)Ph

(1b) (α) R^1=Ph, R^2=C(O)Ph

(1c) (α) R^1=$C_6H_4NO_2$-*p*, R^2=C(O)$C_6H_4NO_2$-*p*

(1d) (α) R^1=Ph, R^2=CH(OH)Ph

(1e) (β) R^1=Ph, R^2=CH_2Ph

(1f) (α) R^1=C_6H_4OMe-*p*, R^2=C(O)C_6H_4OMe-*p*

a R^3=Ph

c R^3=$C_6H_4NO_2$-*p*

Scheme

ketones (40%). It is noteworthy that bond cleavage in the β-isomer (**1a**), in which the carbon–carbon bond to be cleaved is *cis* to the palladium atom, occurs more readily than in the α-isomer (**1b**).

TABLE. The reaction of ketoximes (**1**) with the palladium complex (**2**).

Ketoxime	Product and yield (%)[a]	
	(**3**)	(**4**)
(**1a**)[b]	85	43
(**1b**)[b]	45	11
(**1c**)[b]	68	6
(**1d**)[c]	60	26
(**1e**)[c]	58	46

[a] Yields based on ketoximes. [b] Other products are biphenyls. [c] The corresponding deoximation products[8] were obtained in 25% yield.

In contrast to the ketoximes (**1a**—**e**), ketoximes bearing an electron-donating group are converted into relatively stable palladium complexes, which on heating afford nitriles quantitatively. Thus, the ketoxime (**1f**) gave a yellow complex, m.p. 196–198 °C (decomp.) (50%), which on pyrolysis at 220 °C afforded 4-methoxybenzonitrile (98%). Similarly, 1-oximino-1-phenylpropan-2-one was converted into a pale green-yellow complex, m.p. 249—250 °C (decomp.) (68%), whose n.m.r. spectrum shows aromatic protons around δ 6·67—7·72 (m, 19 H) and methyl protons at 2·50 (3H, d, J_{P-H} 3·8 Hz). The i.r. spectrum (Nujol mull) shows characteristic absorptions at 1650, 1115, and 1190 cm^{-1} ($N \rightarrow O$) and no absorption characteristic of O–H. On pyrolysis of the complex at 250 °C, PhCN was obtained (91%). Although its structural assignment without *X*-ray analysis is premature, a tentative structure, [$PhC(N \rightarrow O)C(O)MePdPPh_2(C_6H_4)$], having a nitrogen–carbon bond has been assigned which is consistent with the analytical data.

This nitrile-forming reaction appears to be different from the deoximation of oximes by the dioxygen complex of palladium.[8] In the latter reaction treatment of (**2**) with molecular oxygen gives the dioxygen complex of palladium which subsequently reacts with the oxime, while in the former, (**2**) reacts first with the oxime to form an intermediate complex which subsequently reacts with molecular oxygen. When the reaction of (**2**) with an oxime is slow, the nitrile-forming reaction and the deoximation compete, and, for aliphatic ketoximes, the deoximation reaction occurs exclusively.

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