

THE MILD DEOXYMATION REACTION OF KETOXIMES WITH THE DIOXYGEN COMPLEX OF PALLADIUM

Kazuyuki Maeda, Ichiro Moritani, Takahiro Hosokawa, and Shun-Ichi Murahashi

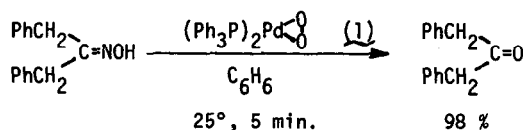
Department of Chemistry, Faculty of Engineering Science, Osaka University
Machikaneyama, Toyonaka, Osaka, Japan 560

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Considerable information concerning to structural studies and inorganic reactions of dioxygen complex of palladium has been considerably accumulated;¹ however, reactions utilizing these complexes for general organic synthesis are sparse.²

We describe here a new efficient procedure of conversion of ketoximes to corresponding ketones by peroxobis(triphenylphosphine)palladium (1). This oxydative deoxygenation reaction can be readily and smoothly carried out under extremely mild conditions which is comparable with those previously developed by utilizing chromous acetate³ and thallium nitrate.⁴

A procedure for the conversion of dibenzyl ketoxime to the ketone follows. To a solution of 1^{5,6} prepared by bubbling molecular oxygen into a solution of tetrakis(triphenylphosphine)-palladium (5.78 g, 5 mmole) in benzene (100 ml) for 30 min was added a solution of dibenzyl ketoxime (1.13 g, 5 mmole) in benzene (20 ml) at ambient temperature. The reaction was complete within 5 min accompanying with precipitation of palladium black. Filtration followed by distillation gave dibenzyl ketone in 98 % yield.



Analogous reactions were generally performed on the other ketones as shown in the Table. Instead of distillation, removing phosphine oxide by filtration over a short column (aluminum or silica gel) gave pure ketones.

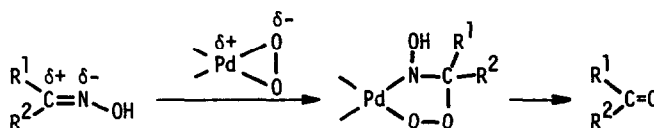
It is noteworthy that the deoxygenation is highly effective in α,β - or γ,δ -unsaturated

ketoimes, and acid- and base-sensitive ketoimes. Since dioxygen complex of palladium is inert to the isolated carbon-carbon double bond, γ,δ -unsaturated ketoimes (e.g. 1-phenyl-4-hexen-1-one) can be effectively converted into the ketones. The deoxygenation of α,β -unsaturated ketoimes (e.g. 1-phenyl-4-methyl-1-penten-3-one)

is slower, but can be accomplished in a moderate yield by using excess complex

1. This trend of reactivity of the complex 1 toward ketoimes is contrast with that of thallium nitrate where oxythallation of α,β -unsaturated ketones is slow compared with isolated carbon-carbon double bonds.⁴ The procedure is unsuccessful only when applied to ketoimes bearing either carbonyl or hydroxyl group in the α -position due to formation of palladium complexes.

The reaction would be envisioned by the 1,3-dipolar cycloaddition of the dioxygen complex 1² with the polar C=N bond of ketoimes as shown in the scheme.



REFERENCES

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TABLE

The Conversion of Ketoimes to Corresponding Ketones^a

Ketones	Yield (%) ^b
Dibenzyl Ketone	98
Benzyl Phenyl Ketone	94
Benzophenone	76
Isopropyl Phenyl Ketone	72
Pinacolone	98
D-Camphor	85
Cyclohexanone	77
2-Methylcyclohexanone	74
1-Phenyl-4-hexen-1-one	59
1-Phenyl-4-methyl-1-penten-3-one	52 ^c

a The reactions were carried out at 25° for 30 min.

b Yields which are not maximum were determined by vpc analyses. c Five times mole of 1 was used.