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CONVENIENT GENERAL SYNTHETIC METHOD FOR 1,4- AND 1,5-DIKETONES BY PALLADIUM CATALYZED OXIDATION OF α-ALLYL AND α-3-BUTENYL KETONES

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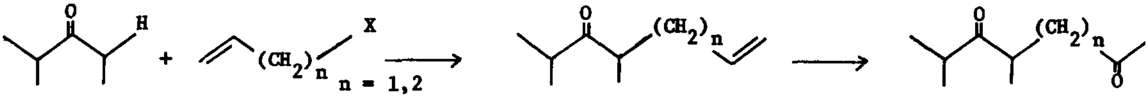
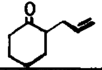
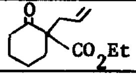
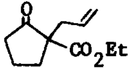
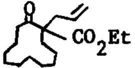
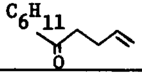
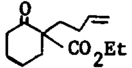
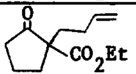
Palladium chloride is a good reagent to oxidize olefins to carbonyl compounds.[1] Industrial production of acetaldehyde from ethylene is a typical example. Despite great industrial success, application of this unique oxidation method to general organic synthesis has not been explored. Only few studies on the oxidation of higher olefins in organic solvents have been reported.[2,3] This paper describes the application of the palladium catalyzed oxidation reaction of terminal olefins to the general synthesis of 1,4-diketones, which are useful starting materials for cyclopentenones and 5-membered heterocyclic compounds. The procedure is based on the allylation of ketones followed by the palladium catalyzed oxidation of the terminal olefin to the methyl ketone.



Allylation of α-position of ketones can be carried out easily in high yields by the well-established enamine method or β-keto ester method. These α-allyl ketones were subjected to oxidation with palladium chloride-cuprous chloride system in DMF under oxygen atmosphere.[4] Usually cupric chloride is used as reoxidant, but we found that cuprous chloride is preferable because cupric chloride tends to chlorinate ketones. In a typical example (Exp.4) cuprous chloride (1 g, 10 mmol) and palladium chloride (0.36 g, 2 mmol) were suspended in DMF (10 ml) and water (1.2 ml). The mixture was placed in a glass vessel used usually for catalytic hydrogenation, and shaken under oxygen atmosphere until absorption of oxygen ceased. Then 2-allyl-2-carbethoxycyclododecanone (2.94 g, mp 56-57°C) was added and the mixture was shaken under oxygen at room temperature for 20 hr. The reaction mixture was poured into 3N hydrochloric acid and the product was extracted with dichloromethane. The crude product was purified by column chromatography (silica gel) and recrystallization (hexane) to give 2-acetonyl-2-carbethoxycyclododecanone (2.30 g, 74%, mp 80-81°C). Results of other experiments are shown in the table (Exp.1-5). Dihydrojasmone was synthesized by this method from 1-undecene-5-one, which was prepared from 2-octanone by magnesium methyl carbonate method[5] (Exp.5).

Similarly 3-butenyl group was introduced to the ketones by the reaction of 3-butenyl bromide. The oxidation of the terminal olefins afforded 1,5-diketones as shown in the table (Exp.6,7). These 1,4- and 1,5-diketones can be identified easily by characteristic nmr spectra. Thus this procedure offers a simple and convenient method for the synthesis of 1,4- and 1,5-diketones.

Exp.	Olefin		$PdCl_2$	CuCl	DMF, H_2O	Time	Yield [a]
1)		5.53 g 40 mmol	0.71 g 4 mmol	3.96 g 40 mmol	20 ml, 2.4 ml	2 hr	3.80 g, 68%
2)		2.52 g 12 mmol	0.35 g 2 mmol	1.0 g 10 mmol	10 ml, 1.2 ml	8 hr	1.99 g, 77%
3)		6.08 g 31 mmol	1.06 g 6 mmol	2.97 g 30 mmol	15 ml, 2.1 ml	24 hr	4.71 g, 71%
4)		2.94 g 10 mmol	0.35 g 2 mmol	1.0 g 10 mmol	10 ml, 1.2 ml	20 hr	2.30 g, 74%
5)		0.47 g 2.8 mmol	0.089 g 0.5 mmol	0.29 g 2.8 mmol	1 ml, 0.1 ml	6 hr	0.34 g, 69%
6)		1.50 g 6.6 mmol	0.18 g 1 mmol	0.5 g 5 mmol	5 ml, 0.6 ml	20 hr	0.91 g, 58%
7)		2.49 g 10.3 mmol	0.35 g 2 mmol	1.0 g 10 mmol	10 ml, 1.2 ml	9 hr	1.84 g, 61%

a) isolated yield of the pure products by distillation or recrystallization

References

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5. M. Stiles, J. Amer. Chem. Soc., 81, 2598 (1959).