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PALLADIUM CATALYZED OXIDATION OF Δ^2, Δ^3, AND Δ^4-UNSATURATED ALCOHOLS

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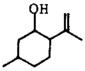
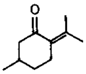
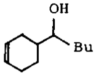
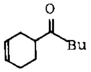
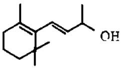
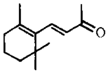
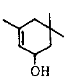
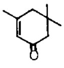
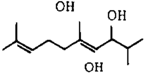
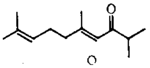
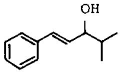
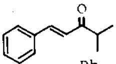
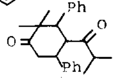
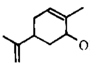
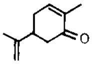
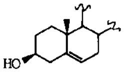
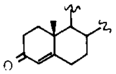
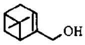
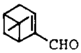
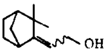
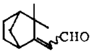
Summary: Palladium (0.6∿3 mol%) catalyzes the oxidation of Δ^2, Δ^3, *and* Δ^4*-unsaturated alcohols to the corresponding ketones in good yields, where bromomesitylene or bromobenzene is used as an oxidant.*

Recently we have reported a very convenient and high yield oxidation of saturated secondary alcohols, where palladium is used as a catalyst and bromobenzene as an oxidant.[1a] In this paper we wish to describe the oxidation of Δ^2, Δ^3, and Δ^4-unsaturated alcohols catalyzed by palladium. As expected,[2] unsaturated alcohols provided the intractable mixtures of arylketones under the conditions reported previously.[1a] In order to circumvent the arylation of double bond, many kinds of oxidants (aromatic halides) and bases were examined and finally we have found that the combination of bromomesitylene and NaH or K_2CO_3 is most satisfactory. The amount of triphenylphosphine relative to palladium acetate is crucial: with 2 equiv of triphenylphosphine the oxidation of isopulegol proceeds smoothly and attains completion within 1 h, while with 1 or 4 equiv of triphenylphosphine the oxidation becomes very sluggish (ca. 10% conversion after 1 h at 50°C, bromomesitylene, NaH). Results are summarized in Table I, which reveals that the present method is applicable to the oxidation of secondary unsaturated alcohols with a wide structural variety. Among alcohols examined, cholesterol is exceptionally reluctant. With bromobenzene the reaciton ceases essentially at 40% conversion. *p*-Methoxy-, *p*-chloro-, and *o*-methylbromobenzene showed no improvement in conversions. Only with bromomesitylene the reaction attains completion in a long reaction time (entry 13). Some successful results of the oxidation of primary allylic alcohols were also listed in Table I.[3,4]

References and Notes

1. (a) Y. Tamaru, Y. Yamamoto, Y. Yamada, and Z. Yoshida, Tetrahedron Lett., 1401 (1979). For the related oxidation, see (b) A. V. Nikiforova, I. I. Moiseev, and Ya. K. Syrkin, Zh. Obsch. Khim., 33, 3239 (1963). C. A., 60, 3995c (1964); (c) W. G. Lloyd, J. Org. Chem., 32, 2816 (1967).

Table I. Oxidation of Δ^2, Δ^3, and Δ^4-Unsaturated Alcohols Catalyzed by Palladium

Entry	Alcohol[a]	Oxidant[d]	Base	Solvent[e]	Temp/Time (°C) (hr)	Conv. (%)	Product	(% yield)[f,g]
1		Mes	NaH	THF	50/1	93		(99)
2		Mes	K_2CO_3	DMF	100/5	95		(70)
3		Ph	NaH	THF	50/3	95		(81)
4		Mes	K_2CO_3	DMF	105/6	88		(77)
5		Ph	K_2CO_3	DMF	105/8	84		(48)[h,i]
6		Mes	K_2CO_3	DMF	100/7.5	86		(65)
7		Mes	NaH	THF	50/6.5	73		(78)[h]
8		Ph	NaH	THF	50/4	93		(75)
9		Mes	K_2CO_3	DMF	100/2.5	100		(66)
10	the same as above	Ph	NaH	THF	50/3.5	100		(80)
11		Mes	K_2CO_3	DMF	100/5.5	98		(90)
12		Ph	K_2CO_3	DMF	105/7.3	85		(58)[h,i]
13		Mes	K_2CO_3	DMF	120/20	92		(98)
14		Ph	K_2CO_3	DMF	120/20	ca. 40		(--)[j]
15[b]		Ph	NaH	THF	65/1	95		(100)
16[c]		Ph	NaH	THF	50/3	98		(100)

(a) Except for entries 15 and 16, usual reaction scale is 3 mmol of alcohol, 3.3 mmol of base, 0.09 mmol of $Pd(OAc)_2$, 0.18 mmol of PPh_3 in 5 ml of solvent. For the general procedure, see ref. 1a. (b) For this run, 1.6 mol% of $Pd(OAc)_2$ and 6.4 mol% of PPh_3 are used. (c) For this run, 0.6 mol% of $Pd(PPh_3)_4$ is used. (d) Mes and Ph are abbreviations of bromomesitylene and bromobenzene, respectively. (e) DMF and THF are used after distillation from CaH_2 and Na-benzophenone, respectively. (f) All new compounds showed satisfactory analytical and spectral data (^1H NMR, IR, Mass). (g) Isolated yield (after Kugelrohr distillation or column chromatography) based on conversion. (h) Vpc yield. (i) In addition to the product indicated, an intractable mixture of phenylated ketones are obtained. (j) Not isolated.

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2. (a) J. B. Melpolder and R. F. Heck, J. Org. Chem., 41, 265 (1976); (b) A. J. Chalk and S. A. Magennis, ibid, 41, 273 (1976); (c) Y. Tamaru, Y. Yamada, and Z. Yoshida, Tetrahedron, 35, 329 (1979) and references cited therein.
3. Unfortunately, the present procedure lacks general applicability for the oxidation of primary allylic alcohols. For example, the oxidation of geraniol has not been successful yet.
4. This work is supported from the Ministry of Education, the Japanese Government (Grant-in-Aid for Scientific Research No. 475663).

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