Oxidation of Steroidal π-Allyl Palladium Chloride Complexes Using Chromium(VI) Oxide in *N,N*-Dimethylformamide†

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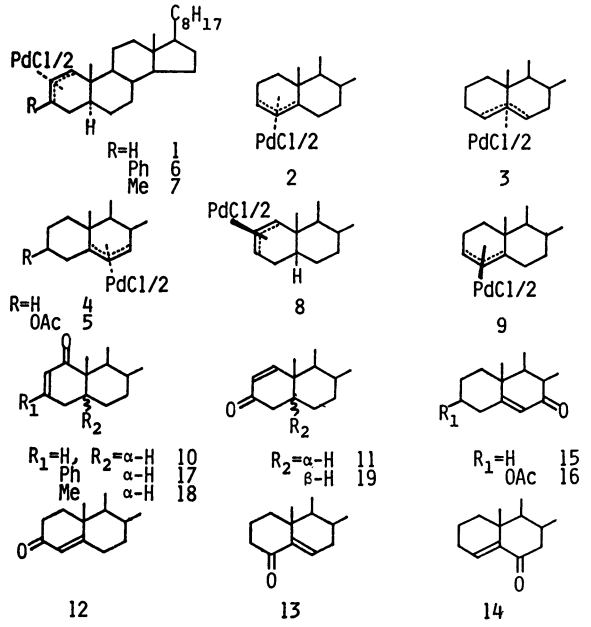
Synopsis. The oxidation of steroidal π-allyl palladium chloride complexes with the mild oxidizing agent composed of chromium(VI) oxide in *N,N*-dimethylformamide containing ether to dissolve the complex and a trace of sulfuric acid, afforded efficiently the corresponding α,β-unsaturated ketones.

It has been reported[1] that the oxidation of π-allyl palladium complexes in the presence of palladium(II) chloride and sodium acetate in aqueous acetic acid gave unsaturated aldehyde or ketone. However, the more heavily substituted π-allyl complexes such as the π-allyl complex of 3-methyl-2-pentene did not react with palladium(II) chloride. The oxidation of π-allyl complexes of the chain compounds[1] and complexes of 1-*p*-menthene[2] with, respectively, sodium dichromate containing sulfuric acid in ether and manganese dioxide containing sulfuric acid in 25% aqueous acetic acid has also been investigated. However, the yields of the α,β-unsaturated ketones were quite low. We have previously reported[3] that the reaction of the cholestene derivatives with palladium(II) chloride in the presence of potassium acetate in acetic acid afforded the corresponding steroidal palladium complexes. Hence, we attempted the oxidation of steroidal π-allyl complexes according to the procedures described by R. Hüttel and H. Christ,[1] G. A. Gray *et al.*,[2] and Jones reagent;[4] but we found that they gave the corresponding α,β-unsaturated ketone and considerable quantities of by-products, namely, carboxylic acids. In the present paper, we would like to report that the oxidation of the steroidal complexes with the mild oxidizing agent[5] composed of chromium(VI) oxide in *N,N*-dimethylformamide containing ether to dissolve the complex and a trace of sulfuric acid, gave the corresponding α,β-unsaturated ketones.



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Results and Discussion

The oxidation of the steroidal π-allyl palladium complexes with chromium(VI) oxide in *N,N*-dimethylformamide and ether, containing a trace of sulfuric acid yielded in all cases the α,β-unsaturated ketones. These ketones were isolated by preparative TLC on silica gel, and identified by comparison with the IR and UV spectral data, and with the melting points of authentic samples. The reaction of di-μ-chloro-bis-[(1-3η-alkyl-5α-cholesten-2α-yl)palladium(II)] (**6**, **7**) gave the 3-alkyl-α,β-unsaturated ketone (**17**, **18**), which showed IR absorptions at 1660 and 1615 cm^{-1} (for R=phenyl); 1673 and 1644 cm^{-1} (for R=methyl). This α,β-unsaturated ketone was determined to be 3-alkyl-5α-cholest-2-en-1-one by means of its NMR spectrum, which showed a singlet at δ 6.10 ppm (CCl_4) (for R=phenyl) and at δ 5.63 ppm ($CDCl_3$) (for R=methyl) due to the olefinic proton.

The results of the oxidation of the steroidal π-allyl complexes are given in Table 1. On the basis of these results, it can be concluded that the mild oxidizing agent

Table 1. Products and isolated yields (%) in oxidation of steroidal π-allyl palladium complexes (**1**—**9**)

Materials	Time / h	Products	Isolated yield/%	Mp / °C
1	5	**10**	28	55—56[6]
		11	38	83—85[7]
2	5	**12**	54	78—81[8]
3	5	**13**	6	108—110[9]
		14	14	100—102[9]
4	5	**15**	62	129—131[10]
5	5	**16**	96	139—145[11]
6	20	**17**[a]	52	213—215
7	20	**18**[b]	64	114—117
8	5	**12**	31	79—81
		19	25	96—99[12]
9	5	**12**	83	78—81

a) IR(KBr): 1660 and 1615 cm^{-1}; λ_{max}^{EtOH} (nm): 219 (ε 8,500) and 281 (ε 15,900); NMR (CCl_4): δ 6.10 ppm (s, 1H) and *ca.* δ 7.2—7.6 ppm (m, 5H). Found: C, 85.94; H, 10.42%. Calcd for $C_{33}H_{48}O$: C, 86.03; H, 10.50%. b) IR (KBr): 1673 and 1644 cm^{-1}; λ_{max}^{EtOH} (nm): 234 (ε 11,400), NMR ($CDCl_3$): δ 5.63 ppm (s, 1H). Found: *m/e* 398.3516. Calcd for $C_{28}H_{46}O$: M, 398.3553.

used in this work is efficient in comparison to the various methods reported in the literature for the oxidation of the steroidal π-allyl complexes. In the case of the α-1-3η-type complex of 5α-cholestene, an oxo group was introduced in the direction of the C_1 and C_3 positions. In the case of the β-1-3η-type complex of 5β-cholestene, the oxidation occurred in the direction of the less hindered C_3 position rather than in the direction of the C_1 position, and formed Δ^1- and Δ^4-3-oxo derivative. In the reaction of the α-1-3η-type complex with a functional group at the C_3 position, the product was Δ^2-1-oxo derivative, and the oxidation occurred more slowly than in the case of a complex possessing no functional group. The α- and β-3-5η-type complex yielded cholest-4-en-3-one, and the α-5-7η-type complex gave the Δ^5-7-oxo derivative, quantitatively.

Experimental

All the melting points are uncorrected. The IR, UV, and NMR spectra were measured using a Hitachi model 215 grating infrared spectrometer, a Hitachi recording spectrophotometer model 323, and a nuclear magnetic resonance spectrometer, Hitachi-Perkin Elmer R-20A, in carbon tetrachloride and in deuteriochloroform with TMS as the internal standard.

General Procedure. A mixture of steroidal π-allyl palladium complex (6.0×10^{-1} mmol), chromium(VI) oxide (3.96 mmol), and *N*,*N*-dimethylformamide–ether (1 : 1) (50 ml) containing a trace of sulfuric acid was stirred at 25 °C for 5—20 h. After the usual work-up, the resultant oil was purified by preparative TLC coated with silica gel (2 mm thick) (E. Merck). Elution with benzene–ether (10 : 1) gave the α,β-unsaturated ketone from ethanol.

Materials. The steroidal π-allyl palladium complexes were synthesized by the methods described in the previous paper.[3]

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