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A New Synthesis of *cis*-Diol from Olefin Using Iodine-Copper(II) Acetate

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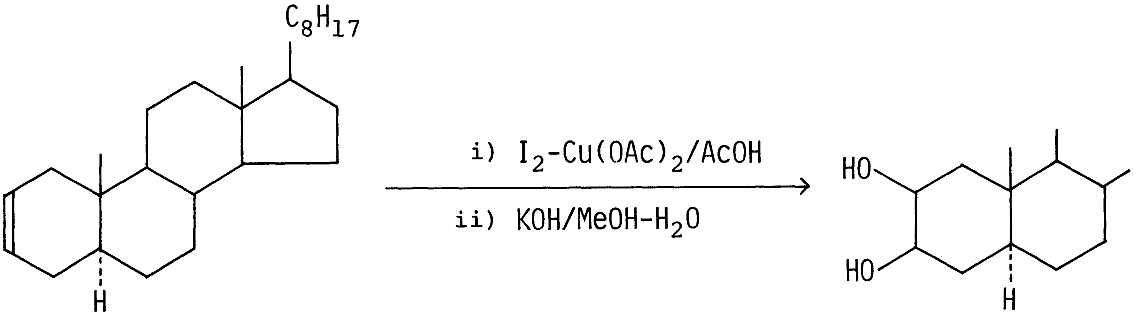
The reaction mixtures of 5α-cholest-2-ene with iodine and copper(II) acetate were converted with potassium hydroxide in methanol-water to give the more hindered 2β, 3β-diol in high yield. Cyclohexene and cycloheptene similarly gave the corresponding *cis*-diols in good yield. This new synthetic method afforded several advantage over the Prévost reaction.

Much work has been reported on the *cis*-hydroxylation of olefins using the Prévost reaction and its Woodward modification.$^{1)}$ These reactions are important methods for the formation of *vic*-diols on the more hindered β-face for 5α-steroid.$^{2)}$ Recently, Cambie *et al.*$^{3)}$ reported that the reaction of olefin with iodine-thallium(I) carboxylate gave the *cis*-hydroxy acetate; and Mangoni *et al.*$^{4)}$ described a convenient method for the preparation of 5α-cholestane-2β, 3β-diol using potassium iodate. Also, Glotter and Schwartz$^{5)}$ reported that the reaction of 5α-cholest-2-ene with thallium(III) acetate in acetic acid gave 5α-cholestane-2β, 3β-diol diacetate and 3-acetate. More recently, Corey and Das$^{6)}$ reported a new method involving the reaction of *trans*-2-bromocyclohexanol with cyanoacetic acid.

We have been investigating a novel iodination using iodine-copper(II) acetate; and as early steps in this research project, we have already reported the α-iodination of ketones;$^{7)}$ the regioselective iodination of estradiol, estriol, and estrone;$^{8)}$ a convenient procedure for the iodination of electron-rich aromatic compounds;$^{9)}$ the α-iodination of carboxylic acid,$^{10)}$ and synthesis of hydroxy-1,4-benzoquinone.$^{11)}$ Previously, we described the syntheses of steroidal *trans*-iodo acetates using iodine-copper(II) acetate in acetic acid.$^{12)}$ Now, in the present paper, we would like to report that the reaction of 5α-cholest-2-ene with iodine-copper(II) acetate is applicable to the synthesis of the more hindered *cis*-diol.

A typical procedure is as follows. A mixture of 5α-cholest-2-ene (1) (500 mg), iodine (690 mg), copper(II) acetate (542 mg), and acetic acid (50 ml) was stirred under refluxing for 3 h. After the usual work-up, the resulting oil yielded reaction mixtures. The reaction mixtures in methanol (50 ml) were treated with potassium hydroxide (50 mg) in water (2.5 ml) under refluxing for 0.5 h. After evaporation of the reaction mixtures, the residue was dissolved in ether. The ethereal solution was washed with water, dried, and evaporated. Crystallization of the residue from methanol gave plates of 5α-cholestane-2β, 3β-diol (4) (491 mg), mp 174-177 °C (175-176 °C$^{5)}$).



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The reaction of cyclohexene (2) and cycloheptene (3) with iodine and copper(II) acetate in acetic acid or propionic acid yielded the corresponding *cis*-diols. These results are summarized in Table 1.

From these results, it was concluded that iodine-copper(II) acetate in acetic acid is a more efficient *cis*-dihydroxylation agent than in propionic acid. It is noteworthy that this reaction may provide us with a new synthetic method for the more hindered *cis*-diols, more convenient than the methods used heretofore.

Table 1. Products and Isolated Yields in the *cis*-Hydroxylation of Olefin with Iodine and Copper(II) Acetate

Materials	Acid	Temperature/°C	Time/h	Products	Isolated yield/%
1	AcOH	reflux	3	4	91
1	EtCOOH	95	50	4	52
2	AcOH	reflux	10	*cis*-1,2-Diol (5)	83
2	EtCOOH	reflux	25	*cis*-1,2-Diol (5)	43
3	AcOH	reflux	15	*cis*-1,2-Diol (6)	80
3	EtCOOH	25	30	*cis*-1,2-Diol (6)	40

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