no appreciable uv chromophore at 240 nm remained. The catalyst was filtered and the solvent was removed under vacuum. Nmr analysis of the residue confirmed the presence of two compounds as an approximate 1:1 mixture.

The residue (0.095 g) was chromatographed using 8 g of basic Al_2O_3. The fraction eluted with Et_2O was crystallized from hexane to give 0.036 g, mp 146–148°. Mixture melting point determination with an authentic sample of 17β-hydroxy-5α,10α-estran-3-one showed no depression. The fraction eluted with EtOAc was crystallized from hexane–$CHCl_3$ to give 0.052 g, mp 178–180°. Mixture melting point determination with an authentic estradiol sample again showed no depression. Both compounds gave nmr spectra identical with those of the authentic samples.

Dehydrogenation of 19-Nortestosterone.—Using the above procedure, 0.05 g of the compound was treated with 0.013 g of Pd–C. Occasionally a small aliquot was removed for monitoring by uv; after 4 hr no appreciable change in the uv maximum was noted. Tlc confirmed the presence of primarily starting material.

Dehydrogenation of 17β-Hydroxy-17α-methyl-9β,10α-estr-4-en-3-one.—Using the above procedure 0.04 g of the 9β,10α compound was treated with 0.010 g of 5% Pd–C. Monitoring the reaction by uv indicated no appreciable change from starting material. After 24 hr of reaction, still no appreciable change in uv was observed. The catalyst was filtered and the solvent was evaporated. Tlc of the residue revealed in addition to starting material only a trace of a more polar substance.

Dehydrogenation of 17β-Hydroxy-17α-methyl-9β,10β-estr-4-en-3-one (4).—Using the standard procedure 0.1 g of 4 was treated with 0.025 g of 5% Pd–C. Uv analysis after 5 min showed no starting material present. After filtration and removal of solvent, the residue was crystallized from isopropyl ether to give 0.050 g of 5: mp 215–216°; nmr ($CDCl_3$) δ 0.95 and 0.96 (s, 3 H each, C-17 and C-18 Me).

Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.43; H, 9.32.

17α-Methyl-9β-estradiol (5).—To a mixture of 0.3 g of 5% Pd–C in 36 ml of AcOH and 4 ml of Ac_2O was added 0.61 g of 8.[7] One equivalent of H_2 was taken up in 15 min in a calibrated atmospheric hydrogenation apparatus. The catalyst was filtered and the solvent was evaporated *in vacuo*. The residue was dissolved in 20 ml of MeOH containing 2 ml of HCl and refluxed for 1 hr. The solution was poured into ice water and the mixture was extracted thoroughly with EtOAc. The combined organic layer was washed in turn with water, saturated $NaHCO_3$ solution, and NaCl solution. After drying (Na_2SO_4) the solvent was evaporated *in vacuo*, and the residue was crystallized from EtOAc–hexane. The first crop of 0.16 g, mp 259–261°, proved to be estrone. The succeeding three crops, 0.195 g, mp 185–190°, were largely the 9β estrone.

To 15 ml of MeMgBr (*ca.* 5 mol) in 30 ml of THF was slowly added a solution of 0.195 g of the 9β ketone in 25 ml of THF. The mixture was stirred under N_2 at the reflux for 18 hr. After the mixture was cooled, excess saturated NH_4Cl solution was added and the mixture was extracted thoroughly with EtOAc. The combined organic layer was washed in turn with water and saturated NaCl solution. After drying (Na_2SO_4) the solvent was evaporated *in vacuo* and the residue was crystallized from benzene to give 0.16 g, mp 216–218°, of 5. Mixture melting point with material previously obtained by dehydrogenation gave mp 215–218°. The nmr spectra were virtually identical.

Aromatization of 17β-Hydroxy-17α-methylestra-4,9(10)-dien-3-one (6).—A solution of 0.29 g of 6 in 100 ml of 3A EtOH was flushed with N_2 and heated to 80°. Then 0.075 g of 5% Pd–C was added and the mixture was stirred while heating continued. The extent of aromatization was followed by uv; most of the chromophore disappeared in 0.5 hr. The catalyst was filtered and the solvent was evaporated *in vacuo*. The residue was crystallized from Et_2O to give 0.19 g of 7, mp 191–193°. Nmr spectrum of the mother liquor showed no trace of the 9β isomer.

Dehydrogenation of 17β-Hydroxy-17α-methylestr-5(10)-en-3-one (9).—Following the usual procedure, 0.29 g of 9 in 100 ml of 3A EtOH was treated with 0.075 g of catalyst for 4 hr. The reaction rate was monitored by uv; no large amount of aromatic formation was observed. The catalyst was filtered and the solvent was evaporated *in vacuo*. Tlc of the residue showed one major spot for the starting material with a trace of impurity.

Dehydrogenation of 1,4-Dihydro-17α-methylestradiol 3-Methyl Ether (10).—Using the standard procedure, 0.29 g of 10 in 100 ml of 3A EtOH and 0.075 g of catalyst were used. The rate of reaction was followed by uv; reaction was stopped at 0.75 hr. After usual handling tlc was run on residue, which indicated that two compounds were formed. The residue was chromatographed on 50 g of Florisil using benzene–EtOAc (10:1) as solvent. The first crystalline fraction was recrystallized from MeOH to give 17α-methylestradiol 3-methyl ether (12), 0.160 g, mp 99–103°. The second fraction of 0.045 g was not crystalline but nmr analysis showed that this was mainly 9.

Dehydrogenation of 1,2-Dihydro-17α-methylestradiol 3-Methyl Ether (11).—Following the procedure of Birch,[9] 0.2 g of 10 was converted primarily to 11 as evidenced by the large uv maximum at 272 nm. This material without isolation was treated with 0.025 g of 5% Pd–C in the usual way. After work-up as for 10, 0.13 g of 12, mp 100–102°, was obtained.

Dehydrogenation of Estra-3,5-diene-3,17β-diol Diacetate (13).—Following the usual conditions, 0.1 g of 13[12] was treated with 0.025 g of 5% Pd–C. The reaction was monitored by uv and showed no appreciable change in uv chromophore in up to 4 hr. Tlc analysis of the residue showed that only starting material was present.

Registry No.—1, 5670-56-4; 4, 20708-78-5; 5, 30541-88-9; 6, 14531-89-6; 7, 302-76-1; 12, 15236-73-4.

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Oxidation and Reduction Reactions Involving Cobalt–Cyano Complexes

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Received November 6, 1970

The catalytic activity of cobalt–cyano complexes has received considerable attention[1,2] since Iguchi first observed that solutions of such complexes absorbed molecular hydrogen and transferred it to a substrate.[3] Recent publications concerned with the oxidation[4,5] and reduction[5,6] of organic compounds promoted by cobalt–cyano complexes prompt us to report related work. Our observations are presented to clarify and expand these recent reports.

This note describes the epoxidation of allyl alcohol by reacting $[(CN)_5CoOOCo(CN)_5]^{6-}$ (1) with hydrochloric acid in the presence of tungstic acid, the oxidation of 1-octene by 1 in acetic acid solvent, and the reduction of sodium methacrylate in the presence of $[Co(CN)_5]^{3-}$ (2) using water as the hydrogen source.

By utilizing a catalyst such as tungstic acid or sodium tungstate we found that allyl alcohol can be epoxidized, under a nitrogen atmosphere, with 1 as the oxygen source. After 1.5 hr at 70–75° and at a pH of 4.5–5.5, a 70% yield of glycidol (based on consumed active oxy-

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gen) was obtained. Oxidations with **1** are not limited to aqueous systems as we were also able to selectively oxidize 1-octene in acetic acid, under a nitrogen atmosphere, with the oxygen again supplied by compound **1**. In the 1-octene case, however, our reaction conditions gave not the epoxide, but rather a 26% yield of 1,2-octanediol diacetate as the only significant product. The diacetate resulted from reaction of the initial product 1,2-epoxyoctane with the acetic acid solvent.

Pregalia and coworkers previously reported[5] the epoxidation of 1-octene with $[Co(CN)_5OOH]^{3-}$ (**3**) dissolved in water or glacial acetic acid. However, because their reactions were carried out in an oxygen atmosphere, complex product mixtures resulted and it was difficult to differentiate autoxidation products from those arising directly from oxygen present in the cobalt complex. By completely excluding atmospheric oxygen we avoided any competing autoxidation reactions and observed quite selective oxidations. Glycidol was the only organic product obtained from allyl alcohol and only traces of products other than 1,2-octanediol diacetate were detected in the 1-octene oxidation.

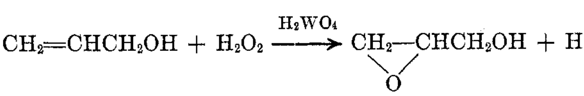
Compound **1** itself is not active as an epoxidizing agent. For example, when the allyl alcohol reaction was repeated in an alkaline medium (pH 9.7-10) only a trace of epoxide formed after 1.5 hr. However, under acidic conditions in water, formation of hydrogen peroxide from **1** apparently occurs *via* **3** as an intermediate. The hydrogen peroxide then epoxidizes the olefin in the presence of tungstic acid. As an additional check of this interpretation, **3** was synthesized, isolated, and reacted with allyl alcohol and sodium tungstate at 70° under alkaline conditions (pH 9-10). Again, no glycidol was formed. Thus **3**, a compound with a hydroperoxy group attached to cobalt, is also inactive as a direct epoxidizing agent. Only under acidic conditions did epoxidation occur. Similarly, Asai and Hara[4] found that **1** was effective in epoxidizing acrolein only after acidification with sulfuric acid. When we used acetic acid as solvent, peracetic acid was most probably the epoxidizing agent.

We propose that the following reactions occur (eq 1-4), in an acidic, aqueous medium, to give epoxidation.

$$2K_3Co(CN)_5 + O_2 \longrightarrow K_3Co(CN)_5OOCo(CN)_5K_3 \qquad (1)$$

$$K_3Co(CN)_5OOCo(CN)_5K_3 + H_2O + H^+ \longrightarrow K_3Co(CN)_5OOH + K_2Co(CN)_5 \cdot H_2O + K^+ \qquad (2)$$

$$K_3Co(CN)_5OOH + H^+ + H_2O \longrightarrow K_2Co(CN)_5 \cdot H_2O + H_2O_2 + K^+ \qquad (3)$$



$$CH_2{=}CHCH_2OH + H_2O_2 \xrightarrow{H_2WO_4} \underbrace{CH_2{-}CHCH_2OH}_{O} + H_2O \qquad (4)$$

Reactions 1-3 have been detailed previously,[7,8] and the use of sodium tungstate or tungstic acid to catalyze allyl alcohol epoxidation by hydrogen peroxide is well documented.[9,10] The combination of reactions 1-3 thus provides a route for the *in situ* generation of hydrogen peroxide from atmospheric oxygen and acid. Additionally, **1** can be generated rather simply, very rapidly, and in good purity (>95%).

We have also found that activated double bonds can be reduced, in the presence of **2**, using water as the hydrogen source. The reaction of **2**, sodium methacrylate, and water at 100° in an autoclave gave a 45% reduction of the unsaturated compound to sodium isobutyrate after 3 hr. After reaction, $K_3Co(CN)_6$ with its strong uv absorptions at 258 and 310 mμ was the only soluble cobalt species indentified. A pink precipitate that formed during the reaction was identified as cobalt hydroxide by X-ray diffraction. These results indicate the ease with which **2** homolytically cleaves a water molecule, a phenomenon that has been noted previously.[11] The hydrido complex thus formed, $K_3Co(CN)_5H$, is responsible for the olefin reduction and for any hydrogen evolved. Our results give further support to the mechanism proposed by Kwiatek, *et al.*,[1,12] for olefin reduction by pentacyanocobaltate. Thus, while two molecules of **2** are necessary to cleave water, only one molecule of $K_3Co(CN)_5H$ is formed and a 50% yield of reduced product (based on the amount of **2** initially present) is the maximum obtainable.

$$K_3Co(CN)_5 + H_2O \rightleftharpoons K_3Co(CN)_5OH + K_3Co(CN)_5H$$

$$K_3Co(CN)_5H + C_3H_5CO_2Na \rightleftharpoons K_3Co(CN)_5(C_3H_6CO_2Na)$$

$$K_3Co(CN)_5(C_3H_6CO_2Na) + H_2O \longrightarrow C_3H_7CO_2Na + K_3Co(CN)_5OH$$

Tarama and Funabiki[6] described the hydrogenation of butadiene by **2** in a glycerine-methanol mixture under a nitrogen atmosphere. The authors suggested that the alcohol solvent was the source of hydrogen for their reduction. Some preliminary work in our laboratory suggests that the rate of olefin reduction in water is many times greater than that in alcohol. This could very well be due to differences in solubility of **2** for its aqueous solutions are homogeneous, unlike the situation in anhydrous methanol. It is quite clear, however, that hydroxylic solvents are the source of hydrogen for reduction in both of these cases.

Experimental Section

Material.—The cobalt-cyano complexes $K_3Co(CN)_5$,[13] $K_6Co_2(CN)_{10}O_2 \cdot H_2O$,[7] $K_3[Co(CN)_5OOH]$,[8] and $Na_6Co_2(CN)_{10} \cdot 4H_2O$[14] were all prepared *via* the reported methods. Careful uv analysis of $K_3[Co(CN)_5OOH]$ indicated it contained 5-10% of $K_2Co(CN)_5 \cdot H_2O$ (uv max 380 mμ) as a contaminant.

Oxidation of Allyl Alcohol.—The epoxidation of allyl alcohol was accomplished by heating 5.2 g of $K_6Co_2(CN)_{10}O_2 \cdot H_2O$ (95-97% pure by iodide titration for active oxygen), 0.8 g of $Na_2WO_4 \cdot 2H_2O$ (or 0.6 g of H_2WO_4), and 7 g of freshly distilled allyl alcohol in 50 ml of degassed water at 70-75° for 1.5 hr under nitrogen. Degassed HCl (1 *N*) was added dropwise during reaction to maintain the pH at 4.5-5.0. After reaction, iodide titration indicated no active oxygen remained and uv analysis no longer showed a uv max at 327 mμ, which is characteristic for $K_6Co_2(CN)_{10}O_2$.[7] Vpc analysis of the reaction mixture showed a 70% yield of glycidol, based on $K_6Co_2(CN)_{10}O_2 \cdot H_2O$. The same reaction was repeated with the pH adjusted to 9.7-10.0, but only a trace of glycidol was formed. Similarly, when 3.4 g of $K_3Co(CN)_5OOH$ was substituted for the $K_6Co_2(CN)_{10}O_2 \cdot H_2O$, no glycidol was formed after 1.5 hr at a pH of 10.

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Oxidation of 1-Octene.—A solution of 11.2 g of 1-octene, 50 ml of degassed glacial acetic acid, and 3.24 g of $K_6Co_2(CN)_{10}O_2$ was heated to 80–85° under nitrogen for 24 hr. After reaction iodide titration indicated that no active oxygen remained. Vpc analysis of the reaction mixture showed a 26% yield of 1,2-octanediol diacetate which was isolated by preparative vpc and identified by its ir and nmr spectra. Only traces of other products were detected by vpc.

Reduction of Sodium Methacrylate.—The reduction of sodium methacrylate was carried cut by reacting 9.8 g of KCN, 7.1 g of $CoCl_2 \cdot 6H_2O$, and 3.2 g of sodium methacrylate in 200 ml of degassed water at 100° for 3 hr in a 300-ml Magnedrive autoclave. After reaction a portion of the reaction mixture was acidified and analyzed by vpc. A 45% yield of isobutyric acid was found. The yellow reaction mixture gave uv maxima at 258 and 310 mμ, corresponding to the reported absorptions for $K_3Co(CN)_6$.[7] A pink precipitate that formed during reaction was identified as $Co(OH)_2$ by its X-ray diffraction pattern.

Registry No.—**1**, 23733-07-5; **2**, 15415-02-8; allyl alcohol, 107-18-6; 1-octene, 111-66-0; sodium methacrylate, 5536-61-8.

Acknowledgments.—The authors wish to express their gratitude to Dr. Thomas Coffield for his stimulating interest and helpful suggestions during the course of this work.

A Convenient Synthesis of 1-Alkynylphosphonates

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Received January 4, 1971

Interest in the preparation of 1-alkynylphosphonates (**3**) was derived from our study of nucleophilic additions to carbon–carbon triple bonds activated by phosphorus(V) groups.[2,3] A literature survey on the preparation of **3** showed that some of the methods reported involve the preparation of explosive alkynyl bromides,[4–6] while other methods are either limited in scope[7] or give low overall yields.[8]

TABLE I

1-ALKYNYLPHOSPHONATES **3**

Series	R	R^1	Bp, °C (mm)	Yield, %	Calcd, % C	Calcd, % H	Calcd, % P	Found, % C	Found, % H	Found, % P
a	CH_3	C_2H_5	82–83 (0.30)[a]	76						
b	n-C_3H_7	C_2H_5	115 (0.20)	59	52.94	8.39	15.16	52.77	8.25	15.04
c	n-C_4H_9	C_2H_5	96 (0.10)[a]	64						
d	n-C_6H_{13}	C_2H_5	133 (0.57)[a]	52						
e	C_6H_5	C_2H_5	132 (0.10)[a]	53						
f	$C_6H_5CH_2CH_2$	C_2H_5	145 (0.05)	60	63.15	7.19	11.63	63.02	7.36	11.80
g	C_6H_{11}	C_2H_5	130 (0.55)	51	59.01	8.67	12.68	58.65	8.86	12.76
h	C_5H_9	C_2H_5	134 (0.90)	70	57.38	8.32	13.45	56.61	8.43	12.89
i	CH_3	C_6H_5	162–163 (0.10)	74	66.78	4.81	11.38	66.04	4.72	11.04
j	n-C_3H_7	CH_3	83 (0.10)	57	47.73	7.44	17.58	47.36	7.46	17.61

[a] Reference 6.

We wish to report a versatile synthesis of **3** starting from alkynylmagnesium bromides (**1**) and dialkyl or diphenyl phosphorochloridates (**2**) (eq 1).

$$\underset{\mathbf{1}}{RC{\equiv}CMgBr} + \underset{\mathbf{2}}{ClP(O)(OR^1)_2} \longrightarrow \underset{\mathbf{3}}{RC{\equiv}CP(O)(OR^1)_2} \quad (1)$$

R = alkyl, cycloalkyl, aryl; R^1 = alkyl, aryl

Some of the compounds **3** produced in this manner are listed in Table I.

The success of this method is easily explained by the reasonable assumption that the chloride ion is more easily displaced than the alkoxide and the phenoxide ion.[9] It is worthwhile to mention that in the preparation of **3i**, we observed traces of phenol in the foreruns of the distillate.

Experimental Section

General Procedure.—Alkynylmagnesium bromide was prepared by stirring 0.05 mol of the alkyne with 0.05 mol of ethylmagnesium bromide in 125 ml of ether at room temperature for 1–2 hr until no more ethane evolved. Dialkyl or diphenyl phosphorochloridate was dissolved in 70 ml of ether and cooled to 0°, and the alkynylmagnesium bromide was added dropwise with continuous stirring. The reaction mixture was stirred at 0° for 1 hr and then at room temperature for 1 hr. Saturated aqueous ammonium chloride solution (100 ml) was added slowly and the phases were separated. The aqueous layer was extracted with ether, the combined ether extract was dried ($MgSO_4$) and evaporated, and the resulting oil was distilled under reduced pressure.

Commercially available diethyl and diphenyl phosphorochloridates were used while dimethyl phosphorochloridate was prepared by passing Cl_2 through a cold solution of dimethyl phosphite in CCl_4.

The ir spectra ($CHCl_3$) of all the compounds **3** listed in Table I show a significant absorption in the region of 4.50–4.60 μ ($C{\equiv}C$); nmr ($CDCl_3$) **3a–h**, doublet of quartets ($J_{HH} = 7$, $J_{PH} = 9$ Hz, δ 4.15–4.20, CH_2O); **3i**, doublet ($J_{PH} = 5$ Hz, δ 1.75, CH_3); **3j**, doublet ($J_{PH} = 13$ Hz, δ 3.88, CH_3O).

Registry No.—**3a,** 1067-88-5; **3b,** 7579-98-8; **3c,** 3450-61-1; **3d,** 3450-66-6; **3e,** 3450-67-7; **3f,** 30238-19-8; **3g,** 30238-20-1; **3h,** 30238-21-2; **3i,** 3095-09-8; **3j,** 30238-23-4.

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