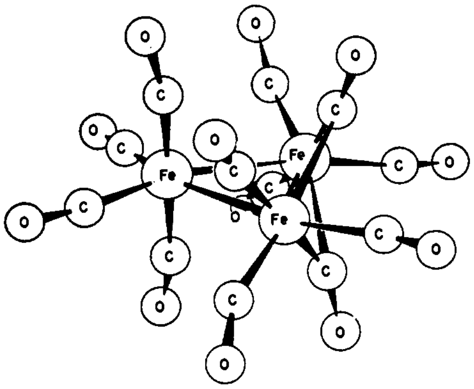
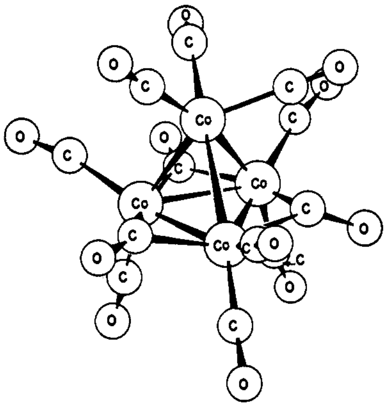


$Fe_3(CO)_{12}$

Figure 1. Molecular configuration of $Fe_3(CO)_{12}$.



$Co_4(CO)_{12}$

Figure 2. Molecular configuration of $Co_4(CO)_{12}$.

triangle are in excellent agreement with the corresponding Fe–Fe distances in $HFe_3(CO)_{11}^-$ (*viz.*, 2.685, 2.696, and 2.577 A with individual esd's of 0.003 A).

A two-dimensional X-ray diffraction study of $Co_4(CO)_{12}$ by Corradini[11] showed that the four cobalt atoms are located at the corners of a regular tetrahedron. From both two-dimensional Fourier maps and stereochemical considerations, Corradini[11] deduced an icosahedral molecular arrangement for the twelve carbonyl groups. However, the lack of resolution in the individual carbonyl groups on the Fourier projections coupled with a crystalline disorder did not make his geometrical assignment of the carbonyl groups unambiguous. Since Corradini[11] did not specify any statistical details, the reliability of his limited structural analysis could not be assessed. Furthermore, other possible alternative molecular models involving different arrangements of carbonyl groups *subsequently* were proposed for $Co_4(CO)_{12}$[12,13]

The reinvestigation of the structure of $Co_4(CO)_{12}$ was prompted by our three-dimensional X-ray studies of $Rh_4(CO)_{12}$[14] and $Ir_4(CO)_{12}$[15] which showed $Ir_4(CO)_{12}$ to be different from $Rh_4(CO)_{12}$ and $Co_4(CO)_{12}$. The tetrameric configuration of $Ir_4(CO)_{12}$ was found to possess approximately T_d cubic symmetry and to be stabilized by *only* iridium–iridium bonds.[15] Although the lattice parameter data of $Rh_4(CO)_{12}$ are similar to those of $Co_4(CO)_{12}$, attempts to determine the complete structure of $Rh_4(CO)_{12}$ were not successful due to a crystal disorder presumably of a different nature from that of $Co_4(CO)_{12}$ as indicated by the different observed space group symmetries for the two compounds.[14] However, Beck and Lottes[16] have shown that $Rh_4(CO)_{12}$ and $Co_4(CO)_{12}$ must have the same over-all molecular structure from the resemblance of their infrared spectra.

Orthorhombic crystals of $Co_4(CO)_{12}$ were prepared, and the crystal data were found to be in agreement with those of Corradini.[11] Three-dimensional photographic intensity data consisting of 529 independent reflections were taken with Mo Kα radiation. After considerable difficulty the entire structure was solved and refined to R_1 and R_2 values of 12.6%.[10]

The *idealized* molecular configuration of C_{3v} symmetry (Figure 2) consists of an apical $Co(CO)_3$ group coordinated by Co–Co bonds to a $Co_3(CO)_9$ fragment containing three identical $Co(CO)_2$ groups situated at the corners of an equilateral triangle with the cobalt atoms linked to one another by both symmetrical bridging carbonyl groups and Co–Co bonds. The twelve carbonyl groups are arranged in an icosahedral array about the tetrahedron of cobalt atoms. This molecular configuration is in agreement with that proposed by Corradini.[11] The six independent Co–Co bond lengths are equivalent within experimental error and have an average value of 2.49 A (individual esd, 0.02 A).

A salient feature is that the approximate molecular configuration of $Fe_3(CO)_{12}$ can be formally derived from that of $Co_4(CO)_{12}$ by the abstraction of a *basal* metal atom from the tetrahedron of cobalt atoms. The relative disposition of the other three metal atoms with respect to the icosahedron of carbonyl groups remains essentially invariant except that this more regular polyhedron in $Co_4(CO)_{12}$ collapses to some extent in $Fe_3(CO)_{12}$ in order that the twelve carbonyl ligands be coordinated to only three iron atoms.

Acknowledgments. We are pleased to acknowledge the financial support of the National Science Foundation. The use of the CDC computers at the Wisconsin Computing Center was made possible through the partial support of NSF and WARF through the University of Wisconsin Research Committee. We also wish to dedicate the structure of $Fe_3(CO)_{12}$ in memory of the late Professor Robert E. Rundle of Iowa State University for his interest and encouragement in this work.

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Direct Fluorination of Steroidal Olefins to *cis*-Vicinal Difluorides

Sir:

It has been shown that elemental fluorine will add smoothly to olefins.[1] The substrate was diluted with an

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inert solvent and the addition was conducted at low temperatures (usually −78°). This procedure has been successful for conjugated olefins such as indene,[1] acenaphthylene,[1] stilbene, and substituted phenanthrenes,[2] as well as for α,β-unsaturated acid halides.[2] *cis* addition was the predominant process with stilbene, acenaphthylene, and the phenanthrenes.[1,2] The only other alternate procedures utilize PbF_4[3] and perhaps $C_6H_5IF_2$[4] and are neither as general nor as simple as one would prefer.

Direct fluorination of Δ^4-cholesten-3-one proceeds smoothly in CCl_3F at −78° to produce the *cis*-4,5-difluoride in yields of 60–70%. The crude adduct mixture was purified from unreacted cholestenone by silica gel chromatography followed by crystallization from methanol and affords the adduct as colorless crystals, mp 187–188°. *Anal.* Calcd for $C_{27}H_{44}F_2O$: C, 76.73; H, 10.49; F, 8.99. Found: C, 76.54; H, 10.76; F, 9.40.

The infrared spectrum of the difluoride contained a carbonyl absorption at 5.72 μ indicative[5] of an α-fluorine substituent. The usual C–F absorption was noted between 8.7 and 9.6 μ. Dehydrofluorination of the adduct (sodium methoxide in methanol) gave 4-fluoro-4-cholesten-3-one, mp 102–103°.[6]

The F^{19} nmr spectrum contained two multiplets centered at ϕ +170.1 and 207.4[7] in an integrated ratio of 1:1. The low-field (ϕ 170.1) multiplet was too complex to interpret and assigned the fluorine atom at C-5. The higher field group (α to the carbonyl) was a pair of doublets with couplings of 47 and 12 cps. The 47 cps coupling is indicative[8] of a geminal J_{HF} and the minor (12 cps) value is assigned as J_{FF}.

The proton nmr spectrum contains two doublets centered at δ 5.0 which are assigned the single C_4 proton geminal to a fluorine atom. The geminal J_{HF} of 47.0 cps is readily apparent. The J_{HF} vicinal then remains with a value of 32.6 cps. This large J_{HF} is sufficient to assign the stereochemistry of the adduct as *cis*.[9] It has been shown[9] that J_{HF} (axial–axial) = 23.4–25.4 cps and J_{HF} (equatorial–axial) = 4.9–11.7 cps in the glycopyranosyl fluorides. *trans*-Diaxial orientation of C_4-hydrogen and C_5-fluorine atoms demands *cis* orientation of fluorine atoms.

The isolated double bond of cholesteryl chloride could also be smoothly fluorinated to the 5,6-difluoride, mp 103–104°. *Anal.* Calcd for $C_{27}H_{45}ClF_2$: C, 73.19; H, 10.24; F, 8.58. Found: C, 73.17; H, 10.55; F, 8.41). The F^{19} nmr spectrum contained a broad band at ϕ +179.7 assigned to the fluorine atom at C_5 and a complex doublet ($J \approx 40$ cps) at ϕ 194.5. The 40 cps value is suggestive of geminal HF coupling[7] and is assigned as the fluorine atom at C_6. The spectrum is too complex to assign this fluorine atom to position 4 where there is only one vicinal proton. The vicinal HF coupling constants could not be obtained since the appropriate region was obscured by the absorption of the proton geminal to the chlorine atom. The stereochemistry is assigned *cis* by analogy with the cholestenone case and the other examples.[1,2,10]

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(7) F^{19} nmr data are given in values of ϕ (ppm from CCl_3F as internal standard).

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(10) The *cis* addition to cholesteryl chloride also is supported by the following observations. Fluorination of cholesteryl acetate gives a low yield (10–20%) of 5α,6α-difluorocholestan-3β-ol acetate, mp 117–118°,[11] F^{19} nmr peaks at ϕ +178.9 and +194 (doublet, geminal $J_{HF} \cong 46$ cps). This acetate was converted by the method of Barnes and Djerassi[11] to 5α,6α-difluorocholestan-3-one, mp 171–172°,[11] F^{19} nmr peaks at ϕ +174.9 and +196 (doublet, geminal $J_{HF} \cong 46$ cps). Direct fluorination of Δ^6-cholesten-3-one has not proceeded satisfactorily.

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2,4-Dinitrophenyl Phosphate

Sir:

The synthesis of 2,4-dinitrophenyl phosphate has eluded the best efforts of a series of investigators.[1] This has led some of them to suppose that the ester must be exceptionally labile, a point of some interest in connection with its possible role in the uncoupling action of dinitrophenol in oxidative phosphorylation.[2]

We have prepared 2,4-dinitrophenyl phosphate in near-quantitative yield by the debenzylation of the dibenzyl ester. This is readily prepared from the phenol and dibenzyl phosphorochloridate in dry ether, in the presence of 1 mole of 2,6-lutidine. After refluxing for 1.5 hr the solution is filtered hot to remove 2,6-lutidine hydrochloride, and the ester crystallizes on cooling. Recrystallization from ether gives colorless crystals, mp 65–66°.

Two grams of the triester is suspended in 50 ml of dry ether and dry HBr passed slowly into the solution at room temperature. After 1.5 hr HBr is no longer absorbed, and a yellow oil has separated. After removal of the solvent, and traces of HBr, *in vacuo*, the residue is dissolved in a large volume of dry ether and 2,6-lutidine added until the solution just turns yellow (1.1–1.2 g). A voluminous white precipitate of the mono-2,6-lutidinium salt is formed. After filtration, and recrystallization from ethanol, this has mp 142° dec. The yield is about 90%. *Anal.* Calcd. for $C_{13}H_{14}N_3O_8P$: C, 42.1; H, 3.77; N, 11.32; P, 8.35. Found: C, 41.7; H, 4.00; N, 11.49; P, 8.29.

One of us has shown previously[3] that a plot of the logarithms of the rate constants for hydrolysis of sub-

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