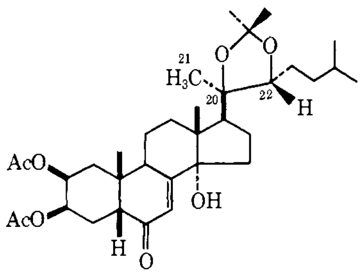
tical with those deduced for the intermediate involved in the cholesterol to pregnenolone conversion.[9]

Treatment of ponasterone A (**3**) 2,3,22-triacetate under vigorous acetylating conditions (acetic anhydride–pyridine, 90°, 20 hr) gave in 50–70% yield the 17,20-ene **4**: powder; nmr ($CDCl_3$) 0.85 (s, 19-H), 0.87 (d, 26- and 27-H), 1.03 (s, 18-H), and *ca.* 5.5 ppm (m, 22-H).[10] The 17,20-ene **4** (100 mg) upon ozonolysis at −80° yielded the methyl ketone **6** (10 mg), oil, together with rubrosterone 2,3-diacetate (**5**) mp 195–198°, exhibiting the same spectral properties as originally reported.[11] The methyl ketone **6** had the following properties: M^+ at *m/e* 186; ir ($CHCl_3$) 1731 cm^{-1} (br); nmr ($CDCl_3$) 0.86 (d, 6 H, $J = 6$ Hz, *i*-Pr), 1.1–1.5 (m, 5 H, CH_2CH_2CH), 2.11 (s, 6 H, OAc and CH_3), *ca.* 5.0 ppm (m, 1 H, C*H*OAc); ORD (EtOH) $[\phi]_{293}$ -1.09×10^3 (trough). The ketol acetate **9** of known configuration was next prepared from L-(−)-leucine (**7**) by conversion to L-leucic acid (**8**)[12] ORD (EtOH) $[\phi]_{226}$ $+2.9 \times 10^3$ (peak). It is well proven that the stereochemistry of the chiral center is retained in this reaction due to neighboring participation of the carboxyl group.[13] The acetate of **8** (300 mg) was then converted to the ketol acetate **9** by the sequence: (1) treatment with sodium bicarbonate to give the sodium salt, (2) reaction with oxalyl chloride, (3) reflux for 3 hr in benzene with dimethylcadmium to yield ketone **9** (30 mg; oil; M^+ at *m/e* 172; ir ($CHCl_3$) 1737 cm^{-1} (br); nmr ($CDCl_3$) 0.95 (d, 6 H, $J = 6$ Hz, *i*-Pr), 1.2–1.8 (m, 3 H, CH_2CH), 2.15 (s, 6 H, OAc and CH_3), *ca.* 5.0 ppm (m, 1 H, C*H*OAc); ORD (EtOH) $[\phi]_{296}$ $+7.32 \times 10^2$ (peak)).

As the α-ketol acetates **6** and **9** differ only by one methylene group, which has no effect on the sign of the Cotton effect, and since the ORD curve of **9** of established *S* absolute configuration is positive, the configuration of **6** having an antipolar ORD curve must be *R*. This applies to all other naturally occurring 20,22-dihydroxyecdysones characterized so far (excepting shidasterone).

As for the configuration of C-20-hydroxylated ecdysones, the *R* configuration was established by nmr experiments. Irradiation of the 20-Me group (1.13 ppm) of ponasterone A 2,3-diacetate 20,22-monoacetonide (**10**),[14] mp 157–159°, resulted in a 13% increase in height of the 22-H (3.63 ppm) resonance without an increment in the integrated area; *i.e.*, disappearance of the small W-type coupling between 21-H and 22-H. This demands a trans relationship between the 20-CH_3 and 22-H in **10** and therefore a 20*R* configuration for ponasterone A. Had the 20-CH_3 and 22-H been in a cis relationship (20*S*), an NOE would have been observed between the 21 and 22 protons rather than a W-type coupling.



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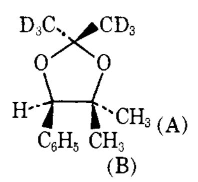

11

This is corroborated by the behavior of (1*R*)-1-phenyl-2-methylpropane-1,2-diol-d_6 acetonide (**11**).[15] Namely, irradiation of the methyl resonance A cis to the 1-methine proton showed an 11% NOE, whereas irradiation of the trans methyl B showed a 16% increase in peak height (W-type coupling) with no increase in integrated area. This situation is the basis of a new simple but rigorous nmr method for determining erythro *vs.* threo configurations of certain glycols and will be described in detail elsewhere.[16]

Thus the 20*R*,22*R* configurations of ponasterone A and other 20-hydroxyecdysones have been unambiguously established.[17,18]

Acknowledgment. We thank Mr. I. Miura, Columbia University, for NOE measurements.

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[10] Geometry of the 17,20-ene is tentatively depicted as in **4** since hydroboration (rear attack) followed by hydrogen peroxide oxidation (20-hydroxyl) and then manganese dioxide oxidation of the 6-allylic alcohol gave a compound having the same retention time as ponasterone A in high-pressure liquid chromatography and tlc. If the product were indeed ponasterone A, the C-20 configuration of which has now been shown to be 20*R*, the double bond configuration of the 17,20-ene would be as shown in **4**. However, the cis–trans isomerism is immaterial for the present deductions.

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[15] This compound was prepared by the reaction of D-mandelic acid methyl ester with excess methylmagnesium bromide, followed by short treatment of the resulting diol with acetone-d_6 and *p*-toluenesulfonic acid catalyst.

[16] D. A. Schooley, M. Koreeda, and K. Nakanishi, to be published.

[17] M. K. acknowledges the Naito Foundation for financial support and D. A. S. acknowledges support of Public Health Service Grant No. GM 44,322 for a postdoctoral fellowship. The research was supported by Public Health Service Grant No. CA-11572. This paper comprises Part XXI on Insect Hormones; for Part XX see M. Koreeda, K. Nakanishi, and M. Goto, *J. Amer. Chem. Soc.*, **92**, 7512 (1970).

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Pentachlorocyclopentadienyl Salts and Organomercury Derivatives. Synthesis and Infrared and Nuclear Quadrupole Resonance Spectra

Sir:

Although the pentachlorocyclopentadienide anion ($C_5Cl_5^-$) has often been mentioned as an intermediate,[1-4] no solid salts of it have been described, nor has

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it been characterized spectroscopically. Our interest in the family of cyclic conjugated chlorocarbons[5] $C_nCl_n^{\pm m}$ has led us to prepare a series of solid salts: $Tl^+C_5Cl_5^-$ (**1**); $Tl^+C_5Cl_5^- \cdot 2C_6H_5CH_3$ (**2**); $R_4N^+C_5Cl_5^-$, where R = n-C_3H_7 (**3a**), n-C_4H_9 (**3b**), or n-C_7H_{15} (**3c**); $(C_2H_5)_3NH^+C_5Cl_5^-$ (**4**); $(n\text{-}C_4H_9)_4P^+C_5Cl_5^-$ (**5**); and $C_5H_5NCH_3^+C_5Cl_5^-$ (**6**). All but **6** are white or colorless salts; **6** is yellow. All are unstable at room temperature, and must consequently be handled by special techniques.

The thallium(I) salts are precipitated by adding a solution of thallium(I) ethoxide to a solution of 1,2,3,4,5-pentachlorocyclopentadiene (C_5Cl_5H) at −78°. If the solvent is hexane, **1** precipitates; from toluene, the adduct **2** crystallizes. The salts **3a**, **3b**, and **3c** may be precipitated at −78° from methanol by (a) adding a solution of the quaternary ammonium hydroxide to C_5Cl_5H, or (b) adding lithium methoxide to a solution of the quaternary ammonium halide and C_5Cl_5H. **5** and **6** are prepared analogously. **4** may be precipitated from ether by adding triethylamine to C_5Cl_5H at −78°.

We also find that stable mercury(II) derivatives of the $C_5Cl_5^-$ anion can be prepared, and wish to report the following: $Hg(C_5Cl_5)_2$ (**7**); C_5Cl_5HgCl (**8**); $C_5Cl_5HgCl \cdot HgCl_2$ (**9**); and $C_6H_5HgC_5Cl_5$ (**10**). Compounds **7**, **8**, and **9** may be prepared by the action of **1** on $HgCl_2$ in THF at −78° in the mole ratios 2:1, 1:1, and 1:2, respectively. The reaction of **1** with C_6H_5HgCl in ether at −78° gives **10**. Unlike the salts, the mercury compounds are stable at room temperature, and have properties indicating that the $Hg-C_5Cl_5$ bond is σ in nature.

Infrared Spectra. Spectra of Nujol mulls of **3b** and **3c** were obtained between 4000 and 250 cm^{-1}. After deleting the cation bands, only two frequencies remained, 1415 (s) and 679 cm^{-1} (s). These disappeared on repeated scanning, as the salt decomposed. Similarly the spectrum of **2** in chloroform solution at −55° shows bands at 1408 (m) and 659 cm^{-1} (s). For any symmetric $(CX)_n$ species, only four vibrational modes are expected to be infrared active,[6] one ring mode and three C–X modes. In hexachlorobenzene the four frequencies are reported at 1345, 694, 217, and 171 cm^{-1}.[7] Hence the spectrum is consistent with a symmetric $(CCl)_5^-$ species.

As expected for the lower symmetry in σ-bonded $C_5Cl_5^-$, the spectra of the mercury compounds contain many more frequencies. Thus the absorptions of **7** (Nujol mull) occur at 1576 (s), 1560 (sh), 1250 (vs), 1200 (m), 1126 (s), 974 (w), 950 (m), 768 (w), 724 (s), 699 (m), 654 (m), and 518 cm^{-1} (vw).

Nuclear Quadrupole Resonance (Nqr) Spectra. The ^{35}Cl nqr spectra of **2**, **5**, and **6** were recorded at 77°K. **5** shows five signals of approximately equal intensity at 35.196, 35.285, 35.334, 35.503, and 35.683 MHz. Similarly, **6** shows lines at 35.016 (intensity 3) and 35.590 MHz (intensity 2). **2** shows a very complex spectrum of about 17 lines, all within the relatively narrow range of 35.95–36.71 MHz. The patterns are consistent with chemical equivalence, but crystallographic nonequivalence, of the chlorines. The frequencies are shifted quite substantially from those in hexachlorobenzene[8] (38.381, 38.452, 38.492 MHz).

Evidently the excess negative charge in the ring is repelled by the lone pairs of the five chlorines, giving a more ionic C–Cl bond and hence a lower nqr frequency. This is also consistent with the reducing nature of the anion, and leads to the prediction that, unlike quite a few chlorocarbons, the $C_5Cl_5^-$ anion should be a charge-transfer *donor*. That this is the case is indicated by the yellow color of the salt **6**, in which the cation is a charge-transfer acceptor.

The nqr spectra of the mercury compounds **7–10** span a much larger frequency range, consistent with the nonequivalence of the chlorines. As an example, **7** shows seven absorptions in the range 36.26–37.06 MHz, assignable to the vinylic chlorines, and two frequencies at 38.86 and 39.06 MHz, assignable to the allylic chlorines. Compounds **8–10** show more complex spectra, but all have resonances in both the vinyl and allyl ranges with relative intensity 4:1.

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Circular Dichroism Induced in Symmetric Cations by Dissymmetric Anions in the Solid State

Sir:

Recently we described a number of effects which were observed when symmetric molecules or racemic molecules were placed in an optically active medium. It was found that the symmetric ion $[PtCl_4]^{2-}$ showed circular dichroism when dissolved in optically active 2,3-butanediol,[1] and similar effects were seen with certain organic ketones and transition metal complexes.[2] Moreover, for the inorganic systems, not only was optical activity induced in the symmetric or racemic systems, presumably through dissymmetric solvation, but the equilibrium constant for the *d* and *l* forms was displaced from unity in the optically active medium.[3] We wish to describe here yet another related phenomenon which is observed in the solid state and which has a significance over and above its observation for the first time.

If the ammine groups freely rotate in the ion $[Co(NH_3)_6]^{3+}$, it is incapable of resolution into optical isomers. However, when the cation is precipitated as the tri[(+)-α-bromocamphor-π-sulfonate] [(+)BCS] salt, $[Co(NH_3)_6]((+)BCS)_3$, the solid dispersed in pressed KBr disks displays clearly detectable circular dichroism in the regions of the first magnetic-dipole-allowed transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$, of the central cobalt(III) ion (Figure 1). Similar effects are observed for the *trans*-$[Co(en)_2Cl_2]$(+)BCS, and *meso-trans*-$[Co(2,3,2\text{-tet})Cl_2]$(+)BCS salts (Figure 2) (where en = ethylenediamine and 2,3,2-tet = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$). In all cases no detectable circular dichroism was observed

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