242 mμ, log ε 4.23). Mild alkaline hydrolysis of V, VI and VII afforded 6α-fluoro compound "S" (VII) (m.p. 203–205°, $[\alpha]_D$ +135°, $\lambda_{\max}$ 236 mμ, log ε 4.21), 6β-fluoro compound "S" (IX) (m.p. 222–224°, $[\alpha]_D$ +14°, $\lambda_{\max}$ 234 mμ, log ε 4.09) and Δ^1-dehydro-6α-fluoro compound "S" (X) (m.p. 210–212°, $[\alpha]_D$ +66°, $\lambda_{\max}$ 241 mμ, log ε 4.22), respectively.

Adrenal incubation[6] of both VIII and X followed by monoacetylation at C-21 gave, in good yield, 6α-fluorohydrocortisone acetate (XI) (m.p. 215–217°, $[\alpha]_D$ +149° (diox.), $\lambda_{\max}$ 237 mμ, log ε 4.23) and 6α-fluoroprednisolone acetate (XII) (m.p. 235–237°, $[\alpha]_D$ +114° (diox.), $\lambda_{\max}$ 242 mμ, log ε 4.25), respectively. Selenium dioxide oxidation[5] of XI gave XII. Chromic acid oxidation of XI and XII provided 6α-fluorocortisone acetate (XIII) (m.p. 215–216°, $[\alpha]_D$ +190°, $\lambda_{\max}$ 233 mμ, log ε 4.21) and 6α-fluoroprednisone acetate (XIV) (m.p. 228–230°, $[\alpha]_D$ +142° (diox.), $\lambda_{\max}$ 237 mμ, log ε 4.23).

An alternative completely chemical route to the 6-fluoro corticoids proceeded from cortisone acetate 3-monoketal (XV).[7] Acetylation of XV at C-17 and peracid epoxidation of the resulting 17,21-diacetate (XVI) (m.p. 180–182°, $[\alpha]_D$ −20°) afforded the 5α,6α-epoxide (XVII) (m.p. 233–234°, $[\alpha]_D$ −18°). Boron trifluoride opening of XVII gave the corresponding 5α-hydroxy-6β-fluoro-3-ketal (XVIII) (m.p. 231–232°, $[\alpha]_D$ −9°) which was directly converted by acid treatment to 6α-fluorocortisone 17,21-diacetate (XIX) (m.p. 270–272°, $[\alpha]_D$ +108°, $\lambda_{\max}$ 233 mμ, log ε 4.20). Alkaline hydrolysis of XIX and subsequent monoacetylation gave XIII. Milder acid treatment of XVIII afforded 6β-fluorocortisone 17,21-diacetate (XX) (m.p. 212–213°, $[\alpha]_D$ +62°, $\lambda_{\max}$ 230 mμ, log ε 4.09).

In the anti-inflammatory and thymolytic assays,[8] 6α-fluorocortisone acetate (XIII), 6α-fluorohydrocortisone acetate (XI), 6α-fluoro-prednisolone acetate (XII) and 6α-fluoroprednisone acetate (XIV) had respective activities of (10,6), (10,8), (20,62), (20,23) times that of hydrocortisone acetate. In the adrenalectomized nonsalt loaded rat XI, XII and XIV promoted sodium excretion.[9]

The details of this work together with the syntheses of other 6-fluoro steroid hormones[4b,10] will be described in future publications.

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[6] A. Zaffaroni, H. J. Ringold, G. Rosenkranz, F. Sondheimer, G. H. Thomas and C. Djerassi, THIS JOURNAL, **80**, October (1958).

[7] R. Antonucci, S. Bernstein, M. Heller, R. Lenhard, R. Littell and J. H. Williams, *J. Org. Chem.*, **18**, 70 (1953).

[8] Anti-inflammatory (cotton pellet implant) and thymolytic activity in adrenalectomized rat, oral route, hydrocortisone acetate = 1. We wish to thank Dr. R. Dorfman of the Worcester Foundation for these assays.

[9] Mineral assays by Dr. R. Dorfman and the Endocrine Labs., Madison, Wisconsin.

[10] By a similar series of reactions there was prepared 6α-fluoro-17α-acetoxy-progesterone (m.p. 249–250°, $[\alpha]_D$ +56°, $\lambda_{\max}$ 236 mμ, log ε 4.21) and 1-dehydro-6α-fluoro-17α-acetoxyprogesterone (m.p. 258–261°, $[\alpha]_D$ +24°, $\lambda_{\max}$ 241 mμ, log ε 4.18) which possess high progestational activity. Thus the former in the Clauberg assay exhibits oral activity equal to 17α-ethynyl-19-nortestosterone (Norlutin).

TRANSPARENT $BaFe_{12}O_{19}$ AND $SrFe_{12}O_{19}$

Sir:

By a solid state reaction of barium fluoride and ferric oxide in the ratio 1:6, under oxygen, a red, transparent, single crystalline form of $BaFe_{12}O_{19}$ was obtained. The hexagonal platelets, approximately 50 microns thick and up to 2 mm. in diameter, are perfectly suitable for the observation and study of Weiss domains, which in the virgin state are about 1 micron wide. As an alternate technique, the reaction of ferric oxide in molten barium chloride or strontium chloride under oxygen, also yielded transparent platelets of $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$. The compositions of the reaction products were established by chemical analysis and single crystal X-ray studies. An apparently similar form of $BaFe_{12}O_{19}$ was described recently by C. Kooy,[1] without indicating the method of preparation.

[1] C. Kooy, *Philips Technical Review*, **19**, 286 (1958).

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THE RADIOLYTIC SYNTHESIS OF THE *cis*- AND *trans*-ISOMERS OF 1,2-DICHLOROETHYLENE OXIDE

Sir:

In the course of some investigations on the radiation chemistry of the symmetrical dichloroethylenes, the *cis* and *trans* forms of 1,2-dichloroethylene oxide have been produced. These compounds have not been reported previously, and in view of the current interest in radiation utilization, we are presenting preliminary data on the radiolytic synthesis and physical properties of these compounds.

The *cis* and *trans* forms of 1,2-dichloroethylene were irradiated in glass cells *in vacuo* with 40-Mev. helium ions impingent on the liquid. After irradiation, the low-boiling products plus the bulk of the 1,2-dichloroethylene were stored in glass-stoppered bottles in the presence of air after preliminary analysis for high-boiling products. In samples that had stood several months, two peaks were found in GLP chromatograms (nonyl phthalate column) that were not present in samples chromatogrammed immediately after irradiation. These peaks were concentrated in the pot liquid by distillation through a small Vigreux column and were further concentrated and purified by running repeat GLP chromatograms of the pot liquid, collecting the respective peaks each time. By this means samples of 1 g. and 0.2 g. of the two respective peak materials were isolated in relatively pure form. These are referred to as dichloroethylene oxide I and dichloroethylene oxide II according to their respective GLP chromatographic emergence times.

The relative yield of oxide I to oxide II from *trans*-1,2-dichloroethylene was about 4.6:1. The ratio from irradiated *cis*-1,2-dichloroethylene was smaller but has not been well determined because of the much lower yield from this isomer.

The compounds isolated have been characterized as the *cis* and *trans* isomers of 1,2-dichloroethylene oxide by mass-spectrometer spectral patterns and by comparison of the infrared spectra with the spectra of the *cis* and *trans* forms of 2,3-epoxybutane. The mass spectra, with parent masses at 112 to 117 mass units, give the empirical formula $C_2H_2Cl_2O$ from isotope ratio arguments. Chemical analysis for C, H, and Cl yielded 21.2%, 1.97%, and 63.5% for oxide I; and 21.2%, 1.92%, and 63.6% for oxide II. The calculated values for $C_2H_2Cl_2O$ are 21.27%, 1.78%, and 62.78%.

Known compounds of this composition, dichloroacetaldehyde and chloroacetyl chloride, were shown to differ from oxide I and oxide II in both mass spectrometer ionization patterns and GLP chromatographic retention times.

The properties, b.p., m.p., $d^{25}{}_4$ and $n^{24}{}_D$ found for these compounds are oxide I: 80–81°, −43°, 1.405 and 1.438; oxide II, 111–112°, −63°, 1.470 and 1.452. From present information it has not been possible to decide unequivocally which compound is the *cis*-isomer and which is the *trans*-isomer.

At present one can only speculate as to the origin of these compounds. Yields of oxide I as high as $G = 9$ were found in old samples of irradiated *trans* 1,2-dichloroethylene. As this is as large as the total yield of "polymer" determined immediately after irradiation, a chain reaction for the formation of the oxides is indicated. An attractive possibility is an auto-oxidation reaction using a long-lived free radical present in very low concentration as the intermediate. Preliminary tests with other sources of radicals (benzoyl peroxide) in the presence of oxygen showed that small yields of both the dichlororethylene oxides are formed from both *cis*- and *trans*-1,2-dichloroethylenes.

This work was performed under the auspices of the United States Atomic Energy Commission.

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SIMPLE METAL ORBITAL TREATMENT OF THE BINDING OF THE HYDROGEN ATOM IN COBALT CARBONYL HYDRIDE

Sir:

On the basis of nuclear resonance and acid dissociation constants, Cotton and Wilkinson[1] have suggested that protons in $HCo(CO)_4$ and $H_2Fe(CO)_4$ are physically close to and primarily bound to the metal atoms. Liehr[2] has discussed which metal orbitals might be used in bonding. Edgell and Gallup[3,4] consider the proton in $HCo(CO)_4$ to be placed so far from the Co atom (~2.0 Å.) that it is primarily bound to the carbon pπ orbitals. This view seems to be based on observed splitting of CO stretching frequencies while corresponding Co–C modes appear unsplit by the proton (according to their assignments). Since such reasoning seems in principle valid, we note that Stammreich[5] has recently observed distinct splittings of *all* triply degenerate vibrations in going from $Fe(CO)_4^{-2}$ to $HFe(CO)_4^-$.

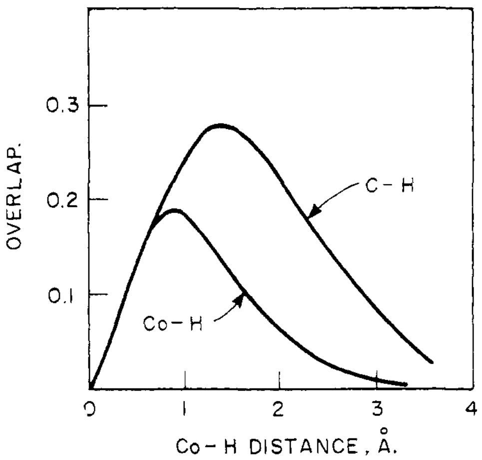

Fig. 1.

In an effort to substantiate their view, Edgell and Gallup[4] reported that a calculation of overlaps shows "that the hydrogen overlap integrals all have a maximum at a Co–H distance just short of 2 Å. . . ."[6] and they call attention to "the relatively large value of the $\phi_H\phi_C$ overlap and the relatively small value of the $\phi_H\phi_{Co}$ overlap." We question whether this type of calculation is as meaningful as they suggest, but granting that it is, there appear to be large numerical errors in their results. Repeating this calculation [(1) placing the hydrogen atom on a C_3 axis of the $Co(CO)_4$ tetrahedron and computing overlaps over the d_{Co-H} range 0.2 to 3.0 Å.; (2) taking S(Co-H) as $S(1s - 3d_{z^2})$; (3) computing for S(C–H) the overlap of the H 1s orbital with a simple LCAO-MO of A_1 symmetry, *viz.*, $1/\sqrt{3}[p\pi_{C_1} + p\pi_{C_2} + p\pi_{C_3}]$; (4) deriving the master formula for $S(1s - 3d_{z^2})$ and using published tables of integrals for Slater orbitals[7]] the results shown in the figure were obtained.

Features of principal interest are: (1) Both the Co–H and C–H overlaps are of comparable magnitude. (2) The C–H overlap maximizes at ~1.4 Å. while the Co–H overlap maximizes at ~0.9 Å. (3) The greatest total overlap (~40% Co–H and ~60% C–H) occurs at $d_{Co-H} \simeq 1.2$ Å. The relative magnitudes of S(Co–H) and S(C–H) could be further altered in favor of S(Co–H) by including overlap in calculating the normalizing factor for the carbon pπ MO and by calculating S(Co–H) using for Co a $3d_{z^2}$–$4p_3$ hybrid orbital. However, taking the results as they are, they suggest that Co–H bonding is quite important and that the hydrogen atom lies within 1.2 Å. of the Co atom. Since the sum of the Co and H radii is 1.2–1.4 Å., it appears not unjustified to describe the proton as somewhat

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[1] F. A. Cotton and G. Wilkinson, *Chemistry and Industry* (*London*), 1305 (1956).

[2] A. D. Liehr, *Z. Naturforsch.*, **12b**, 95 (1957).

[3] W. F. Edgell, C. Magee and G. Gallup, THIS JOURNAL, **78**, 4185 (1956).

[4] W. F. Edgell and G. Gallup, *ibid.*, **78**, 4188 (1956).

[5] H. Stammreich, private communication, to be published shortly.

[6] Note that when $d_{Co\text{-}H} = 2.0$ Å., $d_{C\text{-}H} = \sim 2.2$ Å., *i.e.*, about twice the normal C–H bond distance; yet a total C–H overlap of ~0.64 was reported.[4] It was the improbability of this result which led to the present recalculation.

[7] (a) M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura, *Tables of Molecular Integrals*, Maruzen Co., Tokyo, Japan (1955); (b) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).