tentatively assigned the relative signs of coupling constants in *cis* and *trans* 1-fluoropropene. These studies[6,7] based on high-resolution analyses at several frequencies then establish the relation between the various types of H^1-F^{19} and H^1-H^1 couplings. In both these studies[6,7] it was noted that the *cis* $\text{F} \diagdown \diagup \text{H}$
C=C

coupling, which is a rather small coupling, has the same relative sign as the $\frac{\text{F}}{\text{H}}\text{>C=C}$ coupling and thus a sign reversal takes place for the *cis* coupling on going from trifluoroethylene to derivatives with one fluorine on the double bond.

Subsequent publications from our laboratories will contain the details and discussion of the results of the double resonance studies reported here.

NOTE ADDED IN PROOF.—The assumption made above that the relative signs of the $\text{C—C}<^\text{F}_\text{F}$ and $\text{C=C}<^\text{F}_\text{F}$ couplings are the same has now been verified. From double resonance studies the relative signs of the

coupling constants in
$$\begin{array}{cc} \text{Cl} & \text{F(2)} \\ {}_{(1)}\text{F} \diagdown \text{C=C} \diagup \\ & \text{CFClCFCl}_2 \\ & (3) \quad (4) \end{array}$$
have been

found to be $J_{12}^{\mp}$, $J_{34}^{\mp}$, $J_{23}^{\mp}$, $J_{13}^{\mp}$, $J_{14}^{\pm}$ and $J_{24}^{\pm}$.

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COENZYME Q. XXXVIII. CYCLIZATION OF COENZYME Q TO THE CORRESPONDING CHROMENOLS WITH SODIUM HYDRIDE

Sir:

Quinones of the coenzyme Q group (I–IV) have been converted to the corresponding DL-chromenols (V–VIII) in good yield by a novel procedure, cyclization with sodium hydride. This reaction is of general applicability for preparing DL-chromenols from the coenzyme Q group and for the first time makes these compounds readily available for biological research. Chromenol VII is new, and this reaction will facilitate new syntheses.
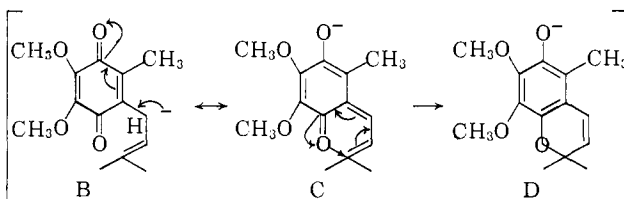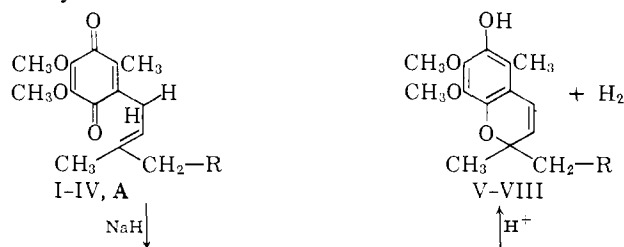
Co Q10 I   R = [CH2CH=C(CH3)CH2]9-H
                 DL-6-chromenol V
Co Q6 II   R = [CH2CH=C(CH3)CH2]5-H
                 DL-6-chromenol VI
Co Q2 III   R = CH2CH=C(CH3)CH3
                 DL-6-chromenol VII
Hexahydro Co Q4 IV R = [CH2CH2CH(CH3)CH2]3-H
                 DL-6-chromenol VIII

The isolation of the 6-chromenol of coenzyme Q_{10} (ubichromenol-50) (V) from human kidney has been reported.[1] Artifactual conversion of coenzyme Q_{10} (ubiquinone-50) (I) during actual and simulated isolation procedures, by saponification of animal tissues[2,3] and upon column chromatography over alumina,[4–7] has been disclosed. Study[3] of the isolation procedure indicated that part of ubichromenol-50 is artifactual, but part may be of natural origin. Although there are other reports of analytical data on ubichromenol in tissues or natural materials, unambiguous proof for the natural occurrence of ubichromenol-50 is not yet available.

Reports on the prevention[8] of the resorption–gestation syndrome in rats by the DL-6-chromenol from coenzyme Q_{10} (V), and the maintenance of motility[9] of chicken sperm by the DL-6-chromenol from hexahydrocoenzyme Q_4 (VIII), gives additional importance to the study of the chromenols.

We[6,8] reported preparation of the chromenols V and VIII from coenzyme Q_{10} and hexahydrocoenzyme Q_4 by conversion on columns of basic alumina; the products were eluted with methanol–ether and purified by chromatography on Florisil or silica gel. The yields were low, 13–38%, and the starting material was hardly recoverable. A new method for the conversion of coenzyme Q to the chromenols has been sought. McHale and Green[10] have just reported that ubiquinone-30 is converted into the corresponding ubichromenol in refluxing pyridine solution.

We have found that coenzyme Q may be converted to chromenols in good yields, 45–90%,[11] by reaction of the quinones with sodium hydride. The quinone was stirred with excess sodium hydride (5.0 molecular equivalents of a 50% sodium hydride dispersion in mineral oil obtained from Metal Hydrides, Incorporated) in refluxing, dry benzene for two hours. Following acidification of the cooled reaction mixture with dilute acetic acid, the benzene layer yielded a residue which was composed primarily of the DL-chromenol, unreacted quinone and mineral oil. Column chromatography on silica gel or Florisil using ether–isoöctane eluents provided purification of the chromenol and recovery of the quinone. Coenzymes Q_{10} (I), Q_6 (II), Q_2 (III) and hexahydrocoenzyme Q_4 (IV) gave the corresponding DL-chromenols: V (*Anal.* Found: C, 81.82; H, 10.80.), VI (*Anal.* Found: C, 78.87; H, 9.64), VII (*Anal.* Found: C, 71.51; H, 8.21) and VIII (*Anal.* Found: C, 75.64; H, 10.63), respectively. Ultraviolet absorption data are given in Table I. N.m.r. data[6] were consistent with the chromenol structures, V–VIII.

The mechanism of this reaction appears to be a base catalyzed cyclization, presumably similar to that[4] for the cyclization of coenzyme Q_{10} over basic alumina.

(1) D. L. Laidman, R. A. Morton, J. Y. F. Paterson and J. F. Pennock, *Biochem. J.*, **74**, 541 (1960).

(2) H. H. Draper and A. S. Csallany, *Biochem. Biophys. Res. Comm.*, **2**, 307 (1960).

(3) F. W. Hemming, D. L. Laidman, R. A. Morton, and J. F. Pennock, *ibid.*, **4**, 393 (1961).

(4) J. Links, *Biochim. Biophys. Acta*, **38**, 193 (1960).

(5) J. Green, E. E. Edwin, A. T. Diplock and D. McHale, *Biochem. Biophys. Res. Comm.*, **2**, 269 (1960).

(6) C. H. Shunk, F. R. Koniuszy, E. L. Wong, N. R. Trenner, B. H. Arison and K. Folkers, *ibid.*, **3**, 228 (1960).

(7) F. W. Hemming, R. A. Morton and J. F. Pennock, *Biochem. J.*, **80**, 445 (1961).

(8) B. C. Johnson, Q. Crider, C. H. Shunk, B. O. Linn, E. L. Wong, and K. Folkers, *Biochem. Biophys. Res. Comm.*, **5**, 309 (1961).

(9) A. C. Page, Jr., M. C. Smith, P. H. Gale, D. Polin and K. Folkers, *ibid.*, **6**, 141 (1961).

(10) D. McHale and J. Green, *Chemistry and Industry*, 1867 (October 27, 1962).

(11) Yields based upon amount of coenzyme Q consumed. Amount of chromenol obtained was 45–60%. Quinone is recovered.

	E_1 $^{1\%}$cm at λ_{max}. μ			
DL-Chromenol	232	274	280	330
V	233	97	92	40
VI	310	126	119	50
VII	598	254	215	101
VIII	382	159	150	65

The activated hydrogen of quinone A is removed as a proton by the hydride ion forming an anion and hydrogen. The anion is considered a resonance hybrid of the resonance structures carbanion B and alkoxide ion C. The alkoxide ion has an electronic configuration suitable for cyclization. Electron shift, initiated by polarization of the carbonyl group, causes cyclization to an aromatic system and gives the phenolate ion D.

The better yields obtained by use of sodium hydride may be due to the "irreversibility" of the first step, and the selectivity of this reagent. Not all of the quinone is converted to the chromenol; apparently part is reduced by the hydride. The resulting hydroquinone is air-oxidized to the quinone during purification. The selectivity of this reagent appears to be unique, and can be appreciated when considering the high reactivity of the methoxy groups. For example, such groups are rapidly replaced by bases, such as the alkoxides[12,13] and amines.

(12) B. O. Linn, N. R. Trenner, B. H. Arison, R. G. Weston, C. H. Shunk and K. Folkers, J. Am. Chem. Soc., **82**, 1647 (1960).

(13) C. H. Shunk, D. E. Wolf, J. F. McPherson, B. O. Linn and K. Folkers, ibid., **82**, 5914 (1960).

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CRYSTALLOGRAPHIC STUDIES OF XeF₂ AND XeF₄[1]

Sir:

The preparation of XeF_4 has been described by Claassen, Selig and Malm.[2] In this study, the existence of a lower fluoride was suggested, and a difluoride, XeF_2, was subsequently prepared by Smith.[3] We wish to report on the structure of XeF_2 prepared by a photochemical process[4] and to present crystallographic data for XeF_4.

XeF_2 is tetragonal with $a = 4.315 \pm 0.003$ Å. and $c = 6.990 \pm 0.004$ A. Space group I4/mmm has been assigned with xenon atoms in 000 and ½½½. This leads to a density value of 4.32 g./cm³. for two molecules in the cell. Single crystal and powder data recorded photographically indicate that the four fluorine atoms are probably in positions $00z$, $00\bar{z}$, $+$ $b.c.$ The very high absorption for the CuKα radiation used in this study and the weak fluorine contributions do not permit an accurate determination of z. However, a value $z = 0.306 \pm 0.020$ produces a noticeable improvement in agreement between calculated and observed intensities. This leads to linear F–Xe–F molecules with Xe–F distances of 2.14 ± 0.14 Å.

Crystals condensed from XeF_4 vapor at room temperature have been found to exhibit more than one symmetry. A monoclinic form frequently observed

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. H. Claassen, H. Selig and J. G. Malm, J. Am. Chem. Soc., **84**, 3593 (1962).

(3) D. F. Smith, J. Chem. Phys., in press.

(4) J. L. Weeks, C. L. Chernick and M. S. Matheson, J. Am. Chem. Soc., **84**, 4612 (1962).

has dimensions $a = 5.03$ Å., $b = 5.92$ Å., $c = 5.79$ Å., and $\beta = 99°27'$. The extinctions, based on single crystal observations with X-rays, correspond to space group P2₁/n. One can account for the intensities generally by placing xenon atoms at 000 and ½½½. Thus, with 2 molecules in the cell, the X-ray density is 4.04 g./cm³. Attempts to locate fluorine positions by X-rays have been unsuccessful because of the very high absorption errors. The assigned space group will permit a planar configuration. However, only a few weak fluorine dependent reflections have been found and one must therefore allow for the possible selection of a different space group. Neutron diffraction data probably will be required in order to locate fluorine positions.

Another form has been found, apparently monoclinic, but distinct from the above modification.

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MOLECULAR SYMMETRY OF XeF₂ AND XeF₄

Sir:

The recent preparation[1] of XeF_2 and XeF_4 has led us to consider the molecular structures of these compounds in terms of a programmed[2] semiempirical LCAO molecular orbital theory. A linear structure for XeF_2 and a square-planar structure for XeF_4 are indicated, as would be expected by analogy to[3,4] $ICI_2{}^{-1}$ and $ICI_4{}^{-1}$. ($IF_4{}^{-1}$, isoelectronic with XeF_4, is known,[5] but its structure is not.)

The basis set consisted of four Slater orbitals of s and p types from each fluorine and nine orbitals of s, p, and d types from xenon. Orbital exponents are $c_s = 2.97$, $c_p = 2.30$, $c_d = 3.71$ for Xe, and $c_s = c_p = 2.42$ for F. Coulomb integrals in e.v. are $Q_s = -30$, $Q_p - 15$, $Q_d = -25$ for Xe, and $Q_s = -31.4$ and $Q_p = -17.4$ for F. The elements of the effective one-electron Hamiltonian matrix $\mathbf{H}$ are related to the overlap matrix $\mathbf{S}$ by

$$H_{ij} = -2(H_{ii}\cdot H_{jj})^{1/2}S_{ij}, \; i \neq j \tag{1}$$

where H_{ii} is the coulomb integral associated with the ith atomic orbital. The eigenvalues λ_j obtained from the solution of

$$\mathbf{H}c = \lambda \mathbf{S}c \tag{2}$$

are used in defining the total orbital energy E as

$$E = \sum_i n_j \lambda_j \tag{3}$$

where n_j is the occupation number (0, 1 or 2) of the jth MO. The bond energy for XeF_n is defined as

$$BE = (1/n)\left(\sum_j m_i H_{ii} - E\right) \tag{4}$$

where the energy of the atoms at infinite separation is taken to be $\sum_i m_i H_{ii}$, with m being the occupation number of the ith AO in the ground state of the free atom.

The results are shown in Table I. Assumption of either smaller xenon exponents or larger (in magnitude) xenon coulomb integrals gave less favorable bonding energies. We consider 16 electron pairs and 17 MO's for XeF_2, while there are 23 electron pairs and 25 MO's for XeF_4. For Xe–F distances taken greater

(1) H. H. Claassen, H. Selig and J. G. Malm, J. Am. Chem. Soc., **84**, 3593 (1962).

(2) T. Jordan, H. W. Smith, L. L. Lohr, Jr. and W. N. Lipscomb, to be published.

(3) R. C. L. Mooney, Z. Krist., **100**, 519 (1939).

(4) R. C. L. Mooney, ibid., **98**, 377 (1938).

(5) G. B. Hargreaves and R. D. Peacock, J. Chem. Soc., 2373 (1960).