The following experiment is typical of the electron-transfer reaction. To 25 ml. of dimethyl sulfoxide-*t*-butyl alcohol (2:1) (all solutions degassed and the reaction conducted under 47 mm. nitrogen pressure), 0.003 *M* in potassium *t*-butoxide, was added 2.01 mmoles of benzenethiol. Nitrosobenzene (1.43 mmoles) was then added, giving a red-brown solution. After stirring magnetically for 35 min., the reaction was quenched with salt solution, then acidified to pH 2 and filtered. Recrystallization of the precipitate from ethanol gave a 70% yield of diphenyl disulfide, m.p. 61°. Other aromatic thiols which undergo oxidation with nitrosobenzene to the disulfide are: (yields in parentheses) *p-t*-butylbenzenethiol (48), thiosalicylic acid (55), *p*-chlorobenzenethiol (60), and *p*-nitrobenzenethiol (58). It is interesting to note that it is conceivable for *p*-nitrobenzenethiol to act as its own electron-transfer agent analogous to the oxidation of *p*-nitrotoluene.[10] It was found that *p*-nitrobenzenethiol and base without any nitrosobenzene gave negligible yields of disulfide utilizing normal (35 min.) reaction times. However, with deficient amounts of base and long reaction times small amounts of disulfide (18% yield in 4 hr.) were formed. If mole to mole amounts of *p*-nitrobenzenethiol and base were used, no disulfide was formed, even with long reaction times. Thus, *p*-nitrobenzenethiol is a poor electron-transfer agent, while its conjugate base undergoes no electron transfer at all.

Our success with nitrosobenzene led us to seek other compounds as electron-transfer agents. Thus it was found that dienophiles such as maleic anhydride and azodicarbonamide with potassium 2-naphthalenethiolate gave high yields of the disulfide. Other possible electron-transfer reagents such as nitrobenzene, acrylonitrile, and acrylamide gave poor yields of the disulfide. The relative electron-transfer ability of these reagents can be determined. Potassium 2-naphthalenethiolate was oxidized with the electron-transfer agent (in the same manner as described for oxidation of potassium benzenethiolate by nitrosobenzene) and the reaction quenched after 1 hr. Ordering the electron-transfer agents in their ability to dimerize potassium 2-naphthalenethiolate we have (yields of the disulfide in parentheses) azodicarbonamide (88) > nitrosobenzene (79) > maleic anhydride (56) >> acrylonitrile (7) > nitrobenzene (6) > acrylamide (0).

Acknowledgment.—The author is indebted to Dr. B. C. Gerstein for many stimulating discussions concerning this work. He is also indebted to Professor G. A. Russell for use of the e.p.r. spectrometer.

amounts of phenylhydroxylamine and nitrosobenzene and (2) the reaction of potassium *t*-butoxide with nitrosobenzene.

　(10) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962).

　(11) Contribution No. 1355. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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Synthesis of Boron Chloroperchlorates and Boron Triperchlorate[1]

Sir:

We have synthesized the compounds BCl_2ClO_4, $BCl(ClO_4)_2$, and $B(ClO_4)_3$ by the reaction of boron trichloride and anhydrous perchloric acid. At −78° the reaction proceeds smoothly with evolution of hydrogen chloride to give a quantitative yield of product and the compound formed is governed by the ratio of boron trichloride to perchloric acid used in the reaction. The

boron chloroperchlorates have also been prepared by an alternative reaction involving boron trichloride and anhydrous silver perchlorate[2] and both methods give identical compounds. These compounds are temperature and moisture sensitive, undergoing hydrolysis and decomposition reactions, but under anhydrous conditions they are stable at low temperatures. Decomposition is accompanied by the eventual evolution of chlorine with the chloroperchlorates of boron losing their chlorine to give compounds containing boron, perchlorate, and oxygen. There is a possibility that in some instances a boroxole triperchlorate is formed as a decomposition product.

Infrared spectra of the boron chloroperchlorates in carbon tetrachloride were obtained and give spectra with sharp, well defined absorption bands corresponding to B–Cl, B–O, and Cl–O bonds. Spectra obtained at −16° and at room temperature on the same solution show no significant change, indicating that these materials are relatively stable in dilute solutions of carbon tetrachloride even at room temperature. In contrast, boron triperchlorate is unstable in carbon tetrachloride at −16°, and as a result a spectrum has not been obtained as yet on this material. Sensitivity of these compounds has made handling tedious, but a low temperature drybox has allowed analytical data and physical properties of these compounds to be measured. These data are summarized in the following sections.

Boron Dichloroperchlorate.—A liquid at −78.5° solidifies to a glassy solid at lower temperatures. *Anal.* Calcd. for BCl_2ClO_4: B, 5.97; Cl, 38.14; ClO_4, 54.89; mol. wt., 181. Found: B, 5.91; Cl, 38.93; ClO_4, 55.15; mol. wt., 180; d^{-16}_4 1.728; $n^{-16}D$ 1.4288. Infrared: B–Cl at 948 and 1002 cm.$^{-1}$.

Boron Chlorodiperchlorate.—A crystalline solid which melts at −15 to −17°: once the compound has melted, recooling results in solidification either to a glassy or a crystalline solid depending on the purity of the compound. *Anal.* Calcd. for $BCl(ClO_4)_2$: B, 4.41; Cl, 14.46; ClO_4, 81.13; mol. wt., 245. Found: B, 4.32; Cl, 14.84; ClO_4, 80.85; mol. wt., 242; d^{-16}_4 1.872; $n^{-16}D$ 1.4348. Infrared: B–Cl band at 1001 cm.$^{-1}$.

Boron Triperchlorate.—A white crystalline solid which does not melt at temperatures up to −5° and undergoes decomposition reactions before its melting point is reached. *Anal.* Calcd. for $B(ClO_4)_3$: B, 3.50; ClO_4, 96.50. Found: B, 3.48; ClO_4, 96.52.

The chloroperchlorates of boron, in addition to being sensitive to heat and moisture, have also shown another type of instability. These compounds readily undergo exchange reactions similar in nature to those observed for the alkyl chloroborinates ($ROBCl_2$ and $(RO)_2BCl$) formed by the reaction of alcohols or phenols with boron trichloride, but exchange is less facile with the perchlorate compounds:

$$2BCl_2ClO_4 \rightleftharpoons BCl_3 + BCl(ClO_4)_2$$
$$3BCl(ClO_4)_2 \rightleftharpoons BCl_3 + 2B(ClO_4)_3$$
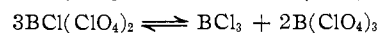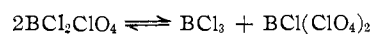
This property makes the purification of the chloroperchlorates by vacuum distillation difficult, since the loss of volatile boron trichloride is a driving force for the reaction. Disproportionation is slow at − 78° under 2–3 mm. pressure, but at 0.1 mm. pressure it proceeds at a measurable rate. Under the latter conditions distillation proceeds rapidly enough so that boron dichloroperchlorate can be distilled leaving behind any boron chlorodiperchlorate formed by the exchange reaction.

Complex formation is a common phenomenon of boron compounds and one case is reported with an organic

perchlorate. Davidson and French[3,4] have prepared diphenylboronium perchlorate [$(C_6H_5)_2BClO_4$] in nitromethane solution by the reaction of diphenylboron chloride and silver perchlorate from which they were able to prepare and isolate an addition compound with 2,2'-dipyridyl. We have prepared a trimethylamine addition compound of boron dichloroperchlorate and have observed enhancement in stability. Direct reaction proceeds with explosive violence, but the reaction can be moderated with suitable solvents. The compound once formed is a white solid which does not melt below 330° and is less sensitive to moisture than the original perchlorate.

(3) J. M. Davidson and C. M. French, J. Chem. Soc., 114 (1958).

(4) J. M. Davidson and C. M. French, Chem. Ind. (London), 750 (1959).

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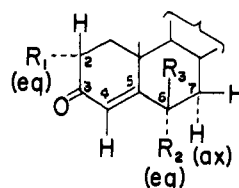SEYMOUR, INDIANA   E. F. MORELLO

Concerning the Steric Requirements for Allylic 1,3-Spin–Spin Fluorine–Proton Coupling[1]

Sir:

The steroid skeleton, by virtue of its rigidity, offers in many instances an ideal structure for determination of the steric requirements for proton–proton[2] or proton–
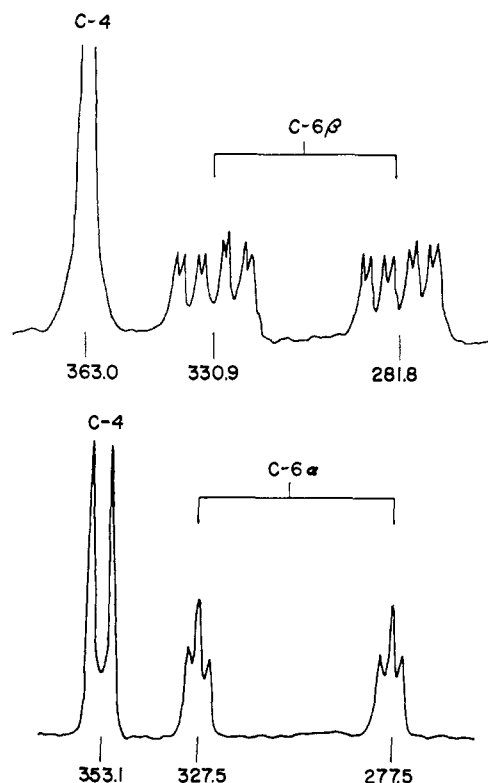

Fig. 1.—The n.m.r. spectra of the C-4 and C-6 protons of the isomeric 6-fluoroandrost-4-ene-3,17-diones determined in CDCl₃ with tetramethylsilane internal standard.[5] Upper curve, 6α-fluoro isomer; lower curve, 6β-fluoro compound.

fluorine[3] spin–spin coupling. Recently it has been demonstrated that in Δ⁴-3-keto steroids the axial 6β-proton but not the equatorial 6α-proton is significantly 1,3-spin–spin coupled to the C-4 vinyl proton.[4]

(1) Supported in part by grants A-4044 and CY-4550, U. S. Public Health Service, and T-185, American Cancer Society.

(2) Cf. K. L. Williamson and W. S. Johnson, J. Am. Chem. Soc., 83, 4623 (1961); F. J. Schmitz and W. S. Johnson, Tetrahedron Letters, 647 (1962); H. J. Ringold, M. Gut, M. Hayano, and A. Turner, ibid., 835 (1962).

(3) A. D. Cross and P. W. Landis, J. Am. Chem. Soc., 84, 1736 (1962); 84, 3784 (1962).

This coupling is manifested in the nuclear magnetic resonance spectrum by the appearance of the vinyl proton as a doublet (J = 1.7–2.0 c.p.s.) when a bromo, chloro, or methyl substituent is present at C-6α and as merely a broad singlet (line width at half-height = 3.4 c.p.s.) when two protons are present at C-6.

We report herein that the spin–spin coupling of an allylic fluorine atom at C-6 with the C-4 vinyl proton appears to exhibit steric dependence identical with the proton–proton examples. A number of 6β-fluoro- (Ia) and 6α-fluoro- (Ib) -Δ⁴-3-ketosteroids have been examined[5] and in each case the 6β-fluorosteroid exhibited for the C-4 proton a doublet centered at about 350 c.p.s.,[5] J = 5–5.5 c.p.s., attributable to fluorine-proton 1,3-coupling. In contrast the C-4 proton of the 6α-fluoro compounds appeared as a single peak at about 360 c.p.s. with an average line width at half-height of 4.5 c.p.s.,[6] the marked broadening being due primarily to unresolved coupling with the 6β-proton and probable coupling of low magnitude with the 6α-fluoro atom.

Ia, R_1=H; R_2=H; R_3=F

b, R_1=H; R_2=F; R_3=H

c, R_1=F; R_2=H; R_3=H

The five 6β-fluoro and eleven 6α-fluoro steroids examined gave essentially similar patterns for the spectral peaks of the C-4 and C-6 protons, but only in the case of the isomeric 6-fluoroandrost-4-ene-3,17-diones was solubility sufficient to allow complete elucidation of the C-6 proton pattern for both isomers. These spectra are therefore reported in detail (Fig. 1). In the 6β-fluoro substance the C-4 proton exhibited a doublet at 350.5 and 355.8 c.p.s. while the C-6α proton appeared as two triplets centered at 277.5 and 327.5 c.p.s. A first-order approximation allows the assignment of $J_{6\beta F,4H}$ = 5.3 c.p.s., $J_{6\alpha H,F}$ = 50 c.p.s., $J_{6\alpha H,7\alpha H}$ = 2.9 c.p.s., and $J_{6\alpha H,7\beta H}$ = 2.9 c.p.s. The 6β-proton of the 6α-fluoro compound appeared as a pair of quartets centered at 281.8 and 330.9 c.p.s.: $J_{6\beta H,6\alpha F}$ = 49.1 c.p.s., $J_{6\beta H,7\alpha H}$ = 11.5 c.p.s., $J_{6\beta H,7\beta H}$ = 5.7 c.p.s. Each of the eight peaks for the 6β proton was further split into a doublet (J = 1.7 c.p.s.) by 1,3-coupling[4] with the C-4 proton. The C-4 proton itself appeared as a single peak at 363 c.p.s.

The 6βF–4H coupling of 5–5.5 c.p.s. is clear-cut and requires no further interpretation. The appearance of the C-4 proton as a broad singlet in the 6α-fluoro case, however, leaves unresolved the degree, if any, of masked 6αF–4H coupling, since it is apparent that even the 6βH–4H coupling of 1.7 c.p.s. has been masked. The possible degree of 6αF–4H interaction has been derived in the following manner. Treating the 6βH, 4H, 6αF atoms as an ABX system with fluorine the X portion, J_{AB} = 1.7 c.p.s. and J_{AX} = 49 c.p.s., the line pattern for the C-4 proton has been calculated[7] assuming various values for J_{BX} (i.e.,

(4) D. J. Collins, J. J. Hobbs, and S. Sternhell, Tetrahedron Letters, 197 (1963); T. A. Wittstruck, S. K. Malhotra, and H. J. Ringold, J. Am. Chem. Soc., 85, 1699 (1963).

(5) Spectra were obtained using a Varian 4300 n.m.r. spectrometer, with field homogeneity control unit, at a frequency of 60 Mc.p.s. The samples were dissolved in deuteriochloroform and the spectra were calibrated using the side-band technique. Peak positions are reported in c.p.s. downfield from tetramethylsilane (internal reference).

(6) The full line widths were measured at half-height and the average line width of the tetramethylsilane reference peak was 1.2 c.p.s. The uncertainty in measurement is estimated to be ±0.2 c.p.s.

(7) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1955, p. 25.